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A reassessment of current volcanic emissions from the Central American arc with specific examples from Nicaragua

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Abstract

The Central American volcanic arc supplies a significant proportion of the persistent annual global sulphur dioxide emissions from volcanoes. In November/December 2003, we completed a survey of the arc section from Mombacho to San Cristóbal in Nicaragua recording individual mean fluxes of 800, 530 and 220 Mg day^{-1} in the plumes from San Cristóbal, Telica and Masaya, respectively. An assessment of fluxes published since 1997 along the entire Central America arc yields a mean total arc flux of SO_2 of 4360 Mg day^{-1} or 8–16% of the annual estimated global volcanic SO_2 flux to the troposphere. New field data shows that Masaya volcano continues to show stable HCl/SO_2 and HF/SO_2 ratios, suggesting a sustained flux of these components of ~220 and 30 Mg day^{-1}, respectively (1997 to 2004). Masaya's plume composition also appears to have been stable, between 2001 and 2003, with respect to all the particulate species measured, with significant fluxes of SO_4^{2-} (4 Mg day^{-1}), Na^+ (0.9–1.3 Mg day^{-1}) and K^+ (0.7 Mg day^{-1}). Extrapolating the Masaya plume species ratios to the entire Central American arc gives mean HCl and HF fluxes of 1300 and 170 Mg day^{-1} and a particulate sulphate flux of 40 Mg day^{-1} for 1997 to 2004, although without further understanding of the degassing processes and sources at depth of these different volatiles, these arc-scale estimates should be treated with caution. Combining our arc scale mean SO_2 flux with published measurements of volcanic gas compositions with respect to CO_2 and H_2O allows us to estimate mean CO_2 fluxes of 4400–9600 Mg day^{-1} and H_2O fluxes of 70,000–78,000 Mg day^{-1} for the arc. Preliminary comparisons of these estimates of outgassing rates with published volatile input fluxes into the Central American subduction zone, suggest that Cl is more efficiently recycled through the subduction zone than CO_2. The results for H_2O are inconclusive.

Keywords: sulphur dioxide; volcanic degassing; volcanic particles; subduction fluxes

1. Introduction

Quantifying volcanic volatile emissions to the atmosphere is of interest both in terms of their impact on the Earth's atmosphere (e.g., Robock and Oppenheimer, 2003) and understanding the way that these species cycle through different reservoirs during processes

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such as subduction (e.g., Wallace, 2005). Different methods have been employed in order to estimate the volcanic outgassing fluxes of different species (e.g., using melt inclusion studies scaled with magma discharge rates or ratios of volatiles to ^{3}He or ^{210}Po, summarised in Hilton et al., 2002; Mather et al., 2003a; Wallace, 2005). However, a common methodology is to combine measurements of the ratio of a species, X, to SO_2 with a relevant volcanic SO_2 flux estimate, as SO_2 is the most comprehensively measured volcanic gas species (due to its low background concentration in the atmosphere and its ease of measurement). This method has been used to make volcanic emissions estimates on global, regional and arc-scales (e.g., Andres and Kasgnoc, 1998; Halmer et al., 2002; Hilton et al., 2002). These emission inventories can then be fed into atmospheric models (e.g., Graf et al., 1997) or used to investigate the different sources and sinks of volatiles during subduction (e.g., Hilton et al., 2002; Wallace, 2005) by attempting to balance the volatile inputs (via subduction of oceanic crust and sediments) and the outputs (via degassing or storage in crustal reservoirs).

In order to calculate reliable volatile fluxes using the method described above, it is necessary to have two things: (i) reliable inventories of volcanic SO_2 emissions from worldwide volcanic centres over time and (ii) reliable estimates of X/SO_2 values for different species. Building reliable inventories of volcanic SO_2 emissions from worldwide volcanic centres over time requires SO_2 flux measurements to be made at the world's sporadically and persistently active volcanoes as frequently as possible. The correlation spectrometer was developed for volcanic applications over 30 years ago and has since provided volcanic SO_2 measurements, via ground-based remote sensing, at many different volcanic centres (Stoiber et al., 1983; McGonigle and Oppenheimer, 2003). More recently, satellite-based instruments and ground-based miniature ultraviolet spectrometers have made important contributions to volcanic SO_2 flux measurement (e.g., Bluth et al., 1993; McGonigle et al., 2002; Carn et al., 2003; Galle et al., 2003). Building a data set of X/SO_2 ratios for different species requires more detailed studies of volcanic emanations via either direct sampling of fumaroles (e.g., using Giggenbach tubes) or plumes emitted from open magma surfaces (e.g., using filter packs) or other remote sensing techniques (e.g., Fourier-Transform Infrared spectroscopy). These measurements are further complicated as while the majority of, for example, chlorine and fluorine is carried in the gas phase of the plume, most metallic species are thought to condense rapidly and to be carried entirely in plume particles (Hinkley, 1991). Therefore to characterise volcanic emissions fully, measurements must be taken of both the plume particle and gaseous phases.

Our study focuses on the Central American volcanic arc, the chain of volcanoes running from Guatemala in the north to Costa Rica in the south. This chain is characterised by a well-defined volcanic front, which is associated with the subduction of the Cocos plate beneath the Caribbean plate (Fig. 1a; Stoiber and Carr, 1973; Carr et al., 2003). Many of these volcanoes are persistently active and strong emitters of SO_2 (those named in Fig. 1a). Andres and Kasgnoc (1998) suggested that Central American volcanoes accounted for about 13% of the total global continuous (as opposed to sporadic short-lived emissions which perturb the total volcanic flux) volcanic SO_2 flux for the period ~1972–1997. Recent studies have presented new SO_2 measurements from volcanoes in Guatemala and El Salvador (Rodríguez et al., 2004) and Costa Rica (Zimmer et al., 2004). By combining these data with new measurements presented here of recent SO_2 fluxes from the Nicaraguan volcanoes between Mombacho and San Cristóbal (Fig. 1b), along with other data from the literature and bulletins of the global volcanism network, we assess the SO_2 degassing of the arc since the compilation of Andres and Kasgnoc (1998). We also present a more detailed analysis of the total volatile emissions (in both the gaseous and particle phases) from the high-temperature plume at Masaya volcano in Nicaragua, updating estimates of Masaya's mean gas-phase plume composition with respect to the hydrogen halides and adding new insights into the fluxes of particle-phase components. Using our updated arc-scale SO_2 degassing flux and measurements (compiled from the literature) of the ratios of the hydrogen halides, CO_2 and H_2O to SO_2 in Masaya's plume, we then make arc-scale estimates of the fluxes of these species due to volcanic degassing. Comparison with published estimates of the rate of input of CO_2, H_2O and Cl into the subduction zone allows us to use our output fluxes to present preliminary estimates concerning the volatile recycling of species such as HCl, CO_2 and H_2O through the Central American arc and to compare these estimates to others made via different methodologies.

2. Methodology

2.1. Remote sensing

During a field campaign in November and December 2003, SO_2 flux measurements were made at some of the volcanic centres along the Central American arc between

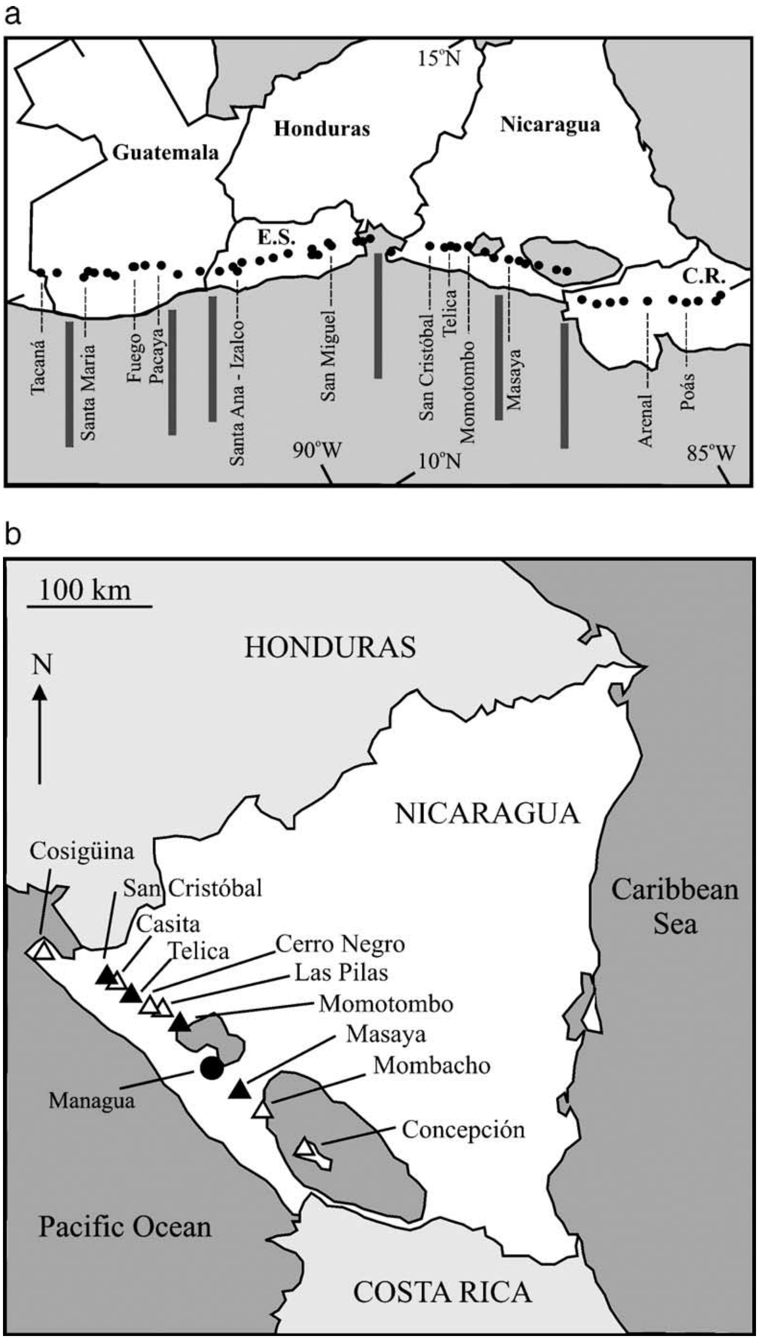

Fig. 1. (a) Map (after Carr et al., 2003) showing the major centres of volcanic degassing (Table 2) along the Central American arc. E.S. is El Salvador, C.R. is Costa Rica. The dark bars mark the approximate boundaries of the volcanic segments as defined in Carr et al. (2003). (b) Map showing the locations of the major volcanoes of Nicaragua. Filled triangles denote the volcanoes at which measurements were taken.

San Cristóbal and Mombacho in Nicaragua. Fluxes were obtained by traversing underneath the plumes, taking measurements of the downward component of scattered solar radiation and analysing it using a Differential Optical Absorption Spectroscopy (DOAS) approach (Galle et al., 2003). The instrumentation included a USB2000 miniature ultraviolet spectrometer (spectral range 245–400 nm, resolution ~0.5 nm, manufactured by Ocean Optics Inc.), coupled to a vertically pointing telescope of 7 mrad field of view with an anti-solarant circular-to-linear converter 4 × 200 μm fibre bundle. Car traverses were achieved using the local road network downwind from each volcano. A USB cable connected the spectrometer to a laptop computer. Software control of the USB2000 was achieved using Jscripts executed in DOASIS software (http://crusoe.iup.uni-heidelberg.de/urmel/doasis/download/) that provided real-time column amount readings, facilitating plume location. Geographic coordinates for each spectrum were obtained using a handheld GPS receiver that logged at 1 Hz via a laptop. Back in the UK, the recorded spectra were re-evaluated using nonlinear fit and optimised fitting windows. These fitting windows were determined in order to obtain a near random residuum with minimal standard deviation (i.e., maximising the fit result). The fitting window varied according to the spectral content of the measured radiation and the degree of cloudiness but was generally 309.63–335.00 nm.

Fluxes were determined from the retrieved SO_2 column amounts and the GPS track by multiplying the distance traversed perpendicular to the plume transport direction corresponding to each spectrum by that spectrum's column amount, summing these products across the whole plume and multiplying by the estimated plume speed. This method has been used to determine SO_2 fluxes from a number of other volcanoes (Stoiber et al., 1983). Measurements were taken at Masaya on the Ticantepe highway on 18 November, 25 November and 1 December 2003 and at San Cristóbal, Telica and Momotombo on the Managua-Chinandega road on 30 November 2003. At San Cristóbal, Telica and Masaya, the measurements were about 5–10 km from each volcano's summit. At Momotombo, they were more distal at about 20–30 km from the volcano's summit. At Masaya, the wind speeds were measured using an anemometer and data logger set up at the highest point on Masaya's crater rim (at approximately plume height and 2 m above ground level). At the other volcanoes, wind speed estimates were obtained by visually tracking plume puffs.

2.2. Errors in the SO_2 flux measurements

There are four components to the error in the SO_2 flux measurements: (i) the error in the retrieved column amount of SO_2, (ii) the error in the distance perpendicular to the plume transport direction determined between adjacent GPS points, (iii) the error in the angle between the assumed wind direction and the traverse path (which affects the projection of the column amount perpendicular to the plume transport direction) and (iv) the error in the plume transport speed. If we denote the SO_2 column amount corresponding to the kth measured spectrum by A_k, the increases in the spectrometer Cartesian coordinates (transformed from the longitude and latitude measured using the GPS via a cylindrical projection taking the crater as the origin) while recording and handling kth spectrum during the traverse as Δx_k and Δy_k, the corresponding traversed distance projected onto the perpendicular to the wind direction as d_k and the plume velocity and direction (angle anti-clockwise from due East) as V and α, respectively, then

$$\Phi_k = V d_k A_k, \text{ where } d_k = -\sin\alpha\Delta x_k + \cos\alpha\Delta y_k$$

where Φ_k is the partial flux, and the total flux, Φ is

$$\Phi = \sum_{k=1}^{N} \Phi_k.$$

Here N is the number of spectra registered beneath the plume. Hence, squared relative error (or squared variation coefficient) can be calculated using error propagation formula as

$$\frac{\sigma_\Phi^2}{\Phi^2} = \sum_{k=1}^{N} \frac{\Phi_k^2}{\Phi^2} \left\{ \frac{\sigma_A^2}{A_k^2} + \frac{\sigma_d^2}{d_k^2} + \frac{(\cos\alpha\Delta x_k + \sin\alpha\Delta y_k)^2}{d_k^2}\sigma_\alpha^2 \right\} + \frac{\sigma_V^2}{V^2},$$

where σ^2 denotes dispersion (the standard deviation squared). In this formula, we have assumed a constant standard deviation of the retrieved SO_2 column amounts and traversed perpendicular distance along the plume i.e., $\sigma_{A_k}^2 = \sigma_A^2 =$constant and $\sigma_{d_k}^2 = \sigma_d^2 =$constant.

The error in the retrieved SO_2 column amount ($\sigma_{A_k}^2$) depends on many factors (Stutz and Platt, 1996; Hausmann et al., 1999) but we assume that the dominant error in terms of flux estimation is the influence of variable cloudiness, which can be approximated as a stationary random process during a particular traverse. Thus, the value of σ_A^2 can be estimated as the standard deviation, σ, of the SO_2 column amount retrieved from the background spectra (i.e., registered outside the plume). From our measurements, we estimate that the error in the column amount contributes ~0.002–0.005 to the squared variation coefficient of the total flux. The error of the distance traversed perpendicular to the plume depends mainly on the GPS precision and can be estimated by performing repeated measurements before and after the traverse at fixed position. These calculations yield a mean contribution to the squared variation coefficient of the total flux of ~0.001–0.003 from this source. In our flux calculations, the wind direction is assumed to be from the volcano's crater to the plume mass centre along the traverse. This assumes both that the plume transport direction is homogeneous and that it is a straight line. The degree of validity of these assumptions is hard to assess for each individual traverse. In order to assess the errors associated with variations in the wind direction, we performed flux calculations for α, $\alpha \pm 3^\circ$ and $\alpha \pm 6^\circ$. The mean contribution to the squared variation coefficient of the total flux is about 0.007 from this source. However, as recognised by Stoiber et al. (1983), the largest single source of error in flux estimates derived via the discussed spectroscopic method arises from uncertainty in the plume speed. For our measurements, we either used ground-based anemometers or visual tracking of plume puffs. It is very difficult to assess the uncertainty of "plume speed" estimates obtained using these methods and the problem is compounded by the complexity of wind fields around volcanoes, which are characterised by high frequency variations in both time and space (Favalli et al., 2004). The plume transport speed relative error is conservatively assumed to be about 25–35%, which is towards the higher end of the range of previous estimates (Stoiber et al., 1983). Our calculations above show that this dominates the other sources of error with the total coefficient of variation of the calculated flux being about 30–40%. This is consistent with the values calculated from the scatter of the recent COSPEC flux measurements reported in Rodríguez et al. (2004). Given the dominance of the error due to the uncertainty in the determination of the plume transport velocity, further efforts to reduce and quantify this error are to be encouraged (e.g., McGonigle et al., 2005). It should also be noted that we disregarded measurements taken when the wind speed was <1.5 m s^{-1} due to the increased errors inherent in such measurements (due to factors such as plume ponding).

Additional error could arise due to multiple scattering (Millán, 1980; Weibring et al., 2002), the presence of volcanic ash in the plume (Andres and Schmid, 2001) or SO_2 depletion. During our field campaign, the plumes always appeared to be bright and free from ash and situated below the clouds, thus we can consider the influence of multiple scattering and ash to be negligible. Losses of SO_2 during transport over the typical distances between emission and measurement at these volcanoes are also assumed to be negligible based on the findings of McGonigle et al. (2004).

2.3. Direct measurements

Filter pack measurements of gases and particles were made at Masaya during the November–December 2003 field campaign, as well as during a previous field campaign in December 2001, by active pumping of air through a serial filter array. In 2001, the sample air stream was first pumped through a 47-mm Nuclepore polycarbonate membrane filter with a 12-μm pore size. At a typical flow rate of 30 l min^{-1}, this retains particles of 2.5 μm with 50% efficiency with the efficiency increasing with increasing particle size. The plume was then passed through a 1-μm pore size 47-mm PTFE filter (Whatman type WTP7590004). This retains all particles with high efficiency, only allowing gases through to the next stage (e.g., Allen et al., 2000). Finally, gases were passed through 2 stages of filters designed to collect acidic gases: 55 mm Whatman 41 ashless circles impregnated with $NaHCO_3$ (10% m/v) and glycerol (1%) in deionised water. In 2003, one 1-μm PTFE particle filter was used to collect all particles. Filters were housed in all-Teflon multiple-stage cartridges (Allen et al., 2000). In 2001, multiple measurements were made, both during the day and night, on the crater rim in Sapper car park downwind of the active vent in Santiago crater. Single measurements were also made at El Panama on the caldera rim ~5 km downwind of the source and just upwind from the Pan American highway ~15 km downwind from the active vent. Background measurements were made in the national park upwind from the vent. Impactor studies of the plume particles were carried out simultaneously (Mather et al., 2003b). In 2003, samples were taken in the daytime in Sapper car park and at the background site.

After sample collection, exposed filters were placed in several layers of small sealable plastic bags, packed in plastic boxes containing an ammonia absorbent (ascorbic acid) to minimise the possibility of acid neutralisation during transit and storage, and returned to the UK for analysis for the major ions SO_4^{2-}, Cl^-, F^-, NO_3^-, H^+, K^+, Na^+, NH_4^+, Ca^{2+} and Mg^{2+} using a pH meter and ion chromatography. The analytical techniques are described in detail elsewhere (Mather et al., 2003b).

3. Results and discussion

3.1. SO_2 flux measurements from Nicaraguan volcanoes

During the 2003 field campaign, measurements were made at major known degassing volcanoes in Nicaragua, namely San Cristóbal, Telica, Masaya, and Momotombo. Although previous episodes of sulphurous degassing have been reported from Las Pilas (e.g., GVN Bulletin, 1994a), Cerro Negro (e.g., GVN Bulletin, 1992, 2003) and Mombacho (e.g., GVN Bulletin, 1994b), this degassing is currently thought to be less significant than the other sources (INETER, 2003) and there was no evidence of coherent plumes from these sources in November–December 2003. San Cristóbal, Telica, Momotombo and Masaya appear in Andres and Kasgnoc's (1998) compilation of continuous SO_2 emitters for 1972–1997 with mean fluxes of 590, 84, 73 and 790 Mg day^{-1}, respectively. A total of 4, 6 and 13 successful traverses were completed at San Cristóbal, Telica and Masaya, respectively, yielding mean fluxes of 800 Mg day^{-1} from San Cristóbal, 530 Mg day^{-1} from Telica and 220 Mg day^{-1} from Masaya (Table 1). Although measurements suggested the presence of SO_2 in Momotombo's plume, its dilute nature (due in part to the greater distance of the road downwind) and the wind conditions at the time meant that we experienced difficulties resolving a coherent plume cross-section and were thus unable to constrain a flux.

As we were only able to make measurements over a very limited period of time, it is important to set our fluxes in the context of other recent measurements and the general pattern of activity at the volcanoes. In Table 2, our new flux measurements for San Cristóbal, Telica, Momotombo and Masaya are compiled with other flux measurements made at these volcanoes since their fluxes were last compiled (Andres and Kasgnoc, 1998). Our new flux measurement from San Cristóbal is consistent with the other reported values since 1997 and the estimated 1972–1997 mean flux (Andres and Kasgnoc, 1998). San Cristóbal's activity has been relatively stable since 1997, with strong fumarolic activity, incandescence within the crater observed at times and occasional mild explosive activity producing varying amounts of ash. At the time of our measurements in November 2003, the seismicity associated with San Cristóbal was relatively low (INETER, 2003). Our new measurement for Telica is consistent with the higher end of the other measurements made since 1997, but is a little higher than the 1972–1997 mean. Reports suggest that activity at Telica has also been relatively stable since 1997, with persistent degassing and seismic activity punctuated by more explosive ash producing events. At the time of our measurements, incandescence was reported in Telica's crater (INETER, 2003). Further measurements are required in order to understand variations in Telica's gas emissions rate. No measurements of Momotombo's SO_2 flux have been reported since the compilation of Andres and Kasgnoc (1998). Reports suggest that its activity has been relatively calm since a period of increased seismicity in 2000, which was accompanied by an increase in the temperature of the crater fumaroles and small increase in the gas emissions (INETER, 2000). It is possible that there has been a decrease in emissions since the measurements compiled in Andres and Kasgnoc (1998) although the lack of reported measurements might also reflect the difficulties of resolving a relatively weak plume from the road. Sulphur dioxide emissions from Masaya have been the most frequently monitored since 1997 of the four volcanoes (Table 2). Emissions have declined since their peak in the late 1990s and are currently comparatively low. Degassing at Masaya is from a lava lake situated down an open-vent in the floor of the crater. At the time of our measurements, activity at Masaya was typical of its recent activity although incandescence from the lava lake was particularly visible. New gas crises or increases in gas flux at Masaya are potentially caused by convective overturns within a long-lived reservoir, bubble-rich layer separation or influx of material from much deeper levels (summarised in Delmelle et al., 1999; Williams-Jones et al., 2003). Progressively lower gas fluxes probably result from progressive depletion of the source magma batch or layer.

3.2. A reassessment of current volcanic emissions from the Central American arc

In Table 2, we compile our new gas flux measurements from Nicaragua with data from other sources along the entire arc in order to reassess the current (since 1997) SO_2 emissions from the Central American arc. The errors in these measurements are assumed to be of the same order as those associated with our measure-

Table 1
Sulphur dioxide fluxes measured (by traversing of the plume from the main active crater at each volcano) from San Cristóbal, Telica and Masaya

Volcano	Date in 2003	Time (UT)[a]	Wind speed (m s^{-1})	SO_2 flux (Mg day^{-1})[b]
San Cristóbal	30 Nov	15:30–17:15	9.6	743, 945, 817, 712 **Mean: 800 ± 190**
Telica	30 Nov	17:45–19:00	9.6	249, 405, 493, 440, 1249, 330 **Mean: 530 ± 120**
Masaya	18 Nov	19:30	1.6	173
	25 Nov	18:00–19:00	1.5–6.8	128, 449, 199, 210, 483
	1 Dec	18:30–19:45	4.2–7.2	262, 179, 141, 137, 238, 178, 129 **Mean: 220 ± 70**

[a] Local time in Nicaragua is UTC −5 h.

[b] Errors are calculated using the coefficient of variation of about 35% estimated in Section 2.2.

Table 2
Compilation of published sulphur dioxide flux measurements for the major persistent SO_2 fluxes from volcanoes on the Central American arc since 1997. Altitudes given in brackets, see Fig. 1a for locations

Volcano	Date	Measured SO_2 flux ($\mathrm{Mg\ day^{-1}}$)	Ref	Comments
Tacaná (4060 m)	*1972–1997 mean*	–	a	Low-temperature fumaroles
	Nov 2001	30	b	
	Mean since 1997	30		
Santa Maria (3772 m)	*1972–1997 mean*	*230*	a	Lava flow and dome extrusion, degassing through high temp. fumaroles.
	Mean Jan/Feb 2001	141	b	
	Jan 2002	106	b	
	Mean since 1997	120		
Fuego (3763 m)	*1972–1997 mean*	*640*	a	
	May–Nov 2001	144	b	Open vent degassing
	Mean Jan–August 2002	406	b	Eruptive phase with lava extrusion
	Mean since 1997	280		
Pacaya (2552 m)	*1972–1997 mean*	*510*	a	
	March 1999	1100	b	
	March–Nov 2000	1500–2000	c	Lava lake and explosions
	Mean Feb/March 2001	1567	b	Almost no extrusion
	Nov 2001	1950	b	Incandescence no longer visible
	Mean Jan 2002	1148	b	
	Mean since 1997	1540		
Santa Ana (2381 m)	*1972–1997 mean*	*20*	a	
	Feb and May 2001	208	b	Heightened activity
	Jan 2002	53	b	
	Mean since 1997	130		
Izalco (4950 m)	*1972–1997 mean*	*20*	a	Fumaroles only emitting steam
	1999	–	d	
	Mean since 1997	–		
San Miguel (2130 m)	*1972–1997 mean*	–	a	Heightened activity
	Jan 2002	260	b	
	Mean since 1997	260		
San Cristóbal (1745 m)	*1972–1997 mean*	*590*	a	Recent activity characterised by strong fumarolic degassing, incandescence within the crater and occasional mild explosive activity.
	Nov/Dec 1999	100–1000	e	
	March 2000	873	f	
	Nov 2003	800	g	
	Mean since 1997	690		
Telica (1061 m)	*1972–1997 mean*	*84*	a	Recent activity characterised by fumarolic degassing with intermittent open-vent and more violent explosive activity.
	March 1997	<40	h	
	Nov 1999	50–500	i	
	Nov 2003	530	g	
	Mean since 1997	280		
Momotombo (1297 m)	*1972–1997 mean*	*73*	a	
	Mean since 1997	–	g	
Masaya (635 m)	*1972–1997 mean*	*790*	a	Persistent open vent degassing punctuated by minor explosions
	Feb–March 1997	390	j	
	Feb–April 1998	1850	j	
	Sept 1998	670	j	
	Feb–March 1999	1790	j	

(continued on next page)

Table 2 (*continued*)

Volcano	Date	Measured SO_2 flux (Mg day^{-1})	Ref	Comments
Masaya (635 m)	March–April 2000	740–1850	k	Persistent open vent degassing punctuated by minor explosions
	April 2000	950	l	
	Jan 2001	360	m	
	Feb 2001	480	m	
	Feb–March 2001	580	m	
	April 2001	346	m	
	Dec 2001	346	n	
	April 2003	691	o	
	Nov/Dec 2003	220	g	
	Mean since 1997	800		
Arenal (1657 m)	*1972–1997 mean*	*110*	a	
	March 2001	180	p	
	Mean since 1997	180		
Poás (2708 m)	*1972–1997 mean*	*500*	a	
	March 2001	8	p	
	Mean since 1997	8		
Arc total 1972–1997		3570 (3720)[q]	a	
Arc total 1997–present day		4320 ± 1500 (4360)[q]		

Conversion factors: 1 Mg day^{-1} = 1 tonne day^{-1} = 0.012 kg s^{-1} .

(a) Andres and Kasgnoc (1998), (b) Rodríguez et al. (2004), (c) GVN Bulletin (2002), (d) GVN Bulletin (1999), (e) GVN Bulletin (2000a), (f) GVN Bulletin (2000b), (g) this work, (h) GVN Bulletin (1997), (i) GVN Bulletin (2000c), (j) Delmelle et al. (1999), (k) GVN Bulletin (2000d), (l) Duffell et al. (2001), (m) Duffell et al. (2003), (n) McGonigle et al. (2002), (o) McGonigle et al. (2004), (p) Zimmer et al. (2004), (q) correcting for unmeasured volcanic fluxes using the power law correction proposed by Brantley and Koepenick (1995).

ments (Rodríguez et al., 2004 includes a more detailed discussion of their COSPEC errors). Crude estimates of the mean flux from each volcano over this period were made by taking the arithmetic mean of all the measurements taken and summed in order to estimate the total SO_2 from the arc.

There are many problems with producing reliable estimates of time-averaged volcanic SO_2 fluxes from intermittently monitored volcanoes. Amongst these issues are sampling problems, for example that measurements are more likely to be made at intermittently monitored volcanoes during periods of heightened activity. It is therefore possible that some of the mean SO_2 measurements detailed in Table 2 represent overestimates of the baseline fluxes from individual volcanoes. It is also hard to be sure that measurements have been made at every degassing volcano along the arc. Brantley and Koepenick (1995) proposed the use of a correction for unmeasured SO_2 fluxes based on an assumed power law distribution of volcanic fluxes on a global scale. This method was applied on a global scale by Andres and Kasgnoc (1998) and used by Hilton et al. (2002) to correct for unmeasured fluxes on arc scales, although the actual fit to the power law distribution in this latter case does not appear to be as close as that for the global data shown in Brantley and Koepenick (1995). Here we have used this approach to correct both the 1972–1997 and then 1997–2004 data sets yielding arc fluxes of 3720 and 4360 Mg day^{-1}, respectively (Table 2). This suggests that ~99% of the arc flux has been measured in our compilation, compared to ~96% in Andres and Kasgnoc's (1998) compilation. Further efforts to cope with sampling issues and to improve the translation of temporally dispersed data sets into meaningful time-weighted means are to be encouraged.

Despite these difficulties, the fact that the total arc flux measurements for the two periods agree to within about 15% which, given the estimated errors in the measurements (see Section 2.2), lends confidence that these fluxes are a good representation of the continuous background flux from the arc. Based on time averaged estimates of global volcanic emissions of ~26,000–55,000 Mg day^{-1} to the troposphere (based on the estimates of total volcanic SO_2 emissions to the atmosphere in Stoiber et al., 1987; Andres and Kasgnoc, 1998; Halmer et al., 2002 corrected for the flux estimated to the stratosphere in Pyle et al., 1996), the recent emissions from the Central American arc account for ~8–16% total volcanic emissions of SO_2 to the troposphere.

Table 3

Mean concentration of major cations and anions in the gas and particle phases of Masaya's plume in 2001 and 2003

	Mean concentration (μg m^{-3})													
	Gas				Particles									
	SO_2	HCl	HF	HNO_3	SO_4^{2-}	Cl^-	F^-	NO_3^-	Na^+	K^+	Mg^{2+}	Ca^{2+}	NH_4^+	H^+
Dec 2001														
Sapper Day (25)	9229.1	1982.2	124.4	170.8	116.2 (93)	11.3 (18)	11.2 (37)	1.24 (40)	30.8 (81)	23.1 (91)	1.5 (36)	6.0 (48)	1.8 (86)	2.8 (79)
Sapper Night (7)	11073.4	1749.3	150.1	206.7	120.1 (91)	19.5 (14)	11.6 (27)	1.9 (32)	50.6 (74)	17.6 (79)	2.2 (22)	5.6 (32)	0.5 (87)	3.2 (81)
El Panama (1)	299.8	75.83	41.6	7.5	6.7 (82)	3.2 (21)	0.8 (38)	0.0 (5)	3.2 (42)	1.2 (86)	0.2 (38)	0.8 (56)	0.5 (98)	0.1 (54)
Pan American (1)	109.5	14.2	9.8	5.0	2.9 (92)	1.1 (28)	0.2 (31)	0.0 (13)	1.4 (44)	0.4 (66)	0.0 (25)	0.4 (25)	0.5 (98)	0.1 (72)
Background (6)	12.2	9.5	10.8	8.2	1.0	1.4	0.0	0.6	1.1	0.4	0.2	0.4	0.2	0.1
Dec/Nov 2003														
Sapper Day (12)	7736.2	1680.0	214.5	607.5	149.2	1.6	3.3	0.3	24.6	20.8	0.9	2.8	1.7	2.1
Background (1)	179.7	11.4	7.7	7.6	2.1	1.8	0.3	1.0	1.1	0.2	0.2	0.5	0.6	0.1

The numbers in brackets after the filter pack description are the number of samples run at that location.

The numbers in brackets after the particle species concentrations are the % of that species in the fine (<2.5 μm diameter) aerosol fraction.

Flow rates were 24–31 l min^{-1} in 2001 and 19–28 l min^{-1} in 2003.

Sampling times were 20–62 min (Sapper), 240 min (El Panama), 365 min (Pan American), 121–370 min (Background) in 2001 and 47–115 min (Sapper), 182 min (Background) in 2003.

Table 4

Fluxes of major cations and anions in gas and particle phases of Masaya's plume (calculated using the SO_2 fluxes summarised in Table 2)

	X									
	Gas		Particles							
	HCl	HF	SO_4^{2-}	Cl^-	F^-	NO_3^-	Na^+	K^+	Mg^{2+}	Ca^{2+}
Dec 2001										
Mean mass ratio (X/SO_2)										
Sapper Day	0.22 ± 0.07	0.01 ± 0.004	0.01 ± 0.004	0.001 ± 0.002	0.001 ± 0.0007	0.0001 ± 0.00012	0.004 ± 0.001	0.003 ± 0.001	0.0002 ± 0.00007	0.0008 ± 0.0004
Sapper Night	0.16 ± 0.02	0.01 ± 0.002	0.01 ± 0.002	0.002 ± 0.001	0.001 ± 0.0004	0.0001 ± 0.00001	0.004 ± 0.005	0.002 ± 0.001	0.0002 ± 0.00004	0.0005 ± 0.0001
El Panama	0.25	0.06	0.02	0.01	0.003	0.0002	0.01	0.003	0.001	0.002
Pan American	0.13	0.09	0.03	0.01	0.002	0.0006	0.01	0.004	0.001	0.003
Flux (Mg day^{-1})[a, b]	**65 ± 33**	**5 ± 2**	**4 ± 2**	**0.6**	**0.4**	**0.0**	**1.3 ± 0.6**	**0.7 ± 0.3**	**0.1**	**0.2**
Nov/Dec 2003										
Mean mass ratio (X/SO_2)										
Sapper Day	0.27 ± 0.19	0.03 ± 0.01	0.02 ± 0.01	0.001 ± 0.001	0.001 ± 0.001	0.0001 ± 0.0003	0.004 ± 0.001	0.003 ± 0.001	0.0001 ± 0.0001	0.0004 ± 0.0002
Flux (Mg day^{-1})[b]	**59 ± 30**	**7 ± 3**	**4 ± 2**	**0.2**	**0.2**	**0.0**	**0.9 ± 0.4**	**0.7 ± 0.3**	**0.0**	**0.1**

NH_4^+ is not included as it is probably not of volcanic origin.

[a] Fluxes are quoted using the mean of the crater rim daytime and nighttime ratios only.

[b] Errors estimated for those volatiles showing significant fluxes assuming 35% error in the SO_2 flux and taking into account the observed standard deviation of the X/SO_2 ratios.

3.3. Other volatile measurements from Masaya

Table 3 shows the mean concentrations of the different species in both the gas and particle phases of Masaya's plume collected in the filter packs at different locations and during the two different sampling periods. In 2001, all the measured species were elevated above background in the near-source plume and SO_2, HCl and particulate SO_4^{2-} were still noticeably elevated in the sample from 15 km downwind. This elevated downwind SO_2 concentration is consistent with, although higher than, the elevated concentrations measured downwind of the active vent using longer exposure time samples (17–27 days) in the same area (Delmelle et al., 2002). For the majority of species, a higher fraction was present in the finer aerosol phase in the daytime plume than in the nighttime plume, probably reflecting enhanced particle growth with the increased nighttime relative humidity, as observed in impactor studies of Masaya's aerosol (Mather et al., 2003b). Sulphate, Na^+, K^+, NH_4^+ and H^+ were more concentrated in the finer aerosol fraction, also consistent with previous studies (Allen et al., 2002; Mather et al., 2003b).

In Table 4, we summarise the mass ratios of the different species to SO_2 and combine these with the SO_2 flux measurements for the two sampling periods to calculate emission rates of the different plume components. There is a high degree of consistency between the daytime near-source ratios for the two measuring periods for all species. This suggests that the plume composition is not only stable over time with respect to HCl/SO_2 and HF/SO_2 ratios (Table 5; Horrocks et al., 1999, 2003) but also with respect to other plume components such as particulate SO_4^{2-}, Na^+, K^+. There also appears to be little variation in the ratios of the plume components between the crater rim and 15 km downwind, consistent with the earlier suggestions that atmospheric processes affect the plume composition to a minimal extent over these length scales (Delmelle et al., 2001; Horrocks et al., 2003; McGonigle et al., 2004). During both measurement periods, the volcano emitted significant fluxes of HCl (59–65 Mg day^{-1}), HF (5–7 Mg day^{-1}), particulate SO_4^{2-} (4 Mg day^{-1}), Na^+ (0.9–1.3 Mg day^{-1}) and K^+ (0.7 Mg day^{-1}), in addition to SO_2.

Although earlier measurements (Stoiber et al., 1986) suggest that there was some variability in Masaya's plume composition in the early 1980s, Table 5 shows that, in terms of HCl, HF and SO_2, the Masaya gas composition has been relatively stable since 1998. Horrocks et al. (1999) explained this stability by an open-system degassing model with deep release of volatiles from the magma and re-equilibration during bubble ascent with the shallow degassed melt prior to emission. This would seem to be supported by the stable composition of the upper layers of the magma pond (represented by microprobe analysis of glasses from Pele's hair and bombs) over timescales several of years (Table 6). Combining the mean SO_2 flux for Masaya since 1997 (800 Mg day^{-1}, Table 2) and the mean hydrogen halide to SO_2 ratios since 1998 (Table 5) suggests mean HCl and HF fluxes from Masaya over this period of 220 and 30 Mg day^{-1}, respectively.

3.4. Fluxes of other volatiles from the Central American arc

Taking together the results of these and previous studies at Masaya as well as at a number of other volcanoes (e.g., Stoiber et al., 1986; Allen et al., 2002; Mather et al., 2004a,b), it is clear that in persistent SO_2-bearing volcanic plumes, a near-source sulphate aerosol of ~1% by mass of the SO_2 is often present. Extending this to the whole arc, it implies a flux of ~40 Mg day^{-1} of sulphate from Central American volcanoes. These fine particles contribute to the background aerosol budget of the atmosphere and may act as effective cloud condensation nuclei (e.g., Mather et al., 2004b) affecting regional cloudiness and precipitation (e.g., Rosenfeld, 1999).

There are few published values of HCl/SO_2 or HF/SO_2 from volcanoes in the Central American arc other than from Masaya. However HCl/SO_2 ratios from Telica for 1981–1982 (mean 0.3 by mass, Stoiber et al., 1986) and Poás (0.2 by mass, GVN Bulletin, 1993) are similar to those from Masaya. The mean value for Masaya since 1998 (0.3 by mass, Table 5) is also very close to the 'Arc Mean' high-temperature volcanic gas composition of $HCl/SO_2 = 0.30$ by mass determined by Gerlach (2004) and to the ratio measured in the plumes from high-temperature degassing at subduction-related andesite-to-dacite (Lascar) and basaltic-to-basaltic-andesite (Villarrica) volcanoes in Chile (Mather et al., 2004b), suggesting that this might be regarded as a reasonable approximation to a 'typical' arc value. If we apply our estimated mean HCl/SO_2 or HF/SO_2 ratios (Table 5) from Masaya to the entire arc, this implies total arc HCl and HF fluxes of 1300 and 170 Mg day^{-1}, respectively, for 1997 to 2004.

Further measurements of halogen degassing along the arc are to be strongly encouraged in order to better constrain these fluxes as we acknowledge that calculat-

Table 5
Summary of recent daytime mass ratio measurements of halogen halide gases and SO_2 for Masaya volcano. For typical errors for filter packs, see Table 4. Fourier Transform Infrared spectroscopy (FTIR) errors were generally of the order of 5–10% (e.g., Duffell et al., 2003)

Volcano	Mean mass ratio		Method and comments	Ref.
	HCl/SO_2	HF/SO_2		
Masaya				
Nov/Dec 2003	0.27	0.03	Filter packs	a
Dec 2001	0.22	0.01	Filter packs	a
May 2001	0.310	0.045	Filter packs and diffusion tubes	b
April 2001	0.124	0.007	FTIR before small explosion	c
2000	0.335	0.079	FTIR	d
1998/1999	0.34	0.04	FTIR	e, f, g
Mean	0.3	0.04		

(a) This work, (b) Allen et al. (2002), (c) Duffell et al. (2003), (d) Duffell et al. (2001), (e) Horrocks et al. (1999), (f) Burton et al. (2001), (g) Burton et al. (2000).

ing hydrogen halide arc degassing fluxes by extrapolation in this way has many potential difficulties. For example:

(i) HCl is highly soluble and any interaction of the volcanic gases with a hydrothermal system will tend to remove HCl from the gas mixture thus reducing the HCl emissions to the atmosphere (e.g., Giggenbach, 1996 and the April 2001 measurements at Masaya before a small phreatomagmatic explosion detailed in Table 5).

(ii) The influence of factors such as magma composition on the solubility of halogens, and the potential release of hydrosaline fluids from magmas is complex and still under investigation (e.g., Carroll and Webster, 1994; Webster et al., 1999; Webster, 2004).

(iii) There may be other arc-scale trends that could potentially affect the proportions of the different volatile components emitted along the arc. For example, along-arc trends in elemental and isotopic ratios (e.g. Ba/La, U/Th, B/La, $^{10}Be/^{9}Be$ and $^{87}Sr/^{86}Sr$) in Central American lavas suggest that the maximum contribution of fluids from subducting marine sediments or altered MORB along the Central American arc occurs in Nicaragua (Patino et al., 2000; Carr et al., 2003). This subduction signal decreases rapidly both to the north and the south and may reflect enhanced fluid release from subducted serpentinised mantle within the highly fractured and flexured slab beneath Nicaragua (Rüpke et al., 2002; Abers et al., 2003; Ranero et al., 2003). While the balance in contributions to the sulphur in arc magmas from the depleted mantle wedge; and sulphur entering the subduction zone from altered oceanic crust, serpentinised oceanic mantle or subducting sediment is poorly understood (e.g., Alt and Shanks, 2003; Alt et al., 2003; Henson et al., 2003), previous studies have suggested that the majority of Cl and H_2O may derive from the subducted slab component (e.g., Straub and Layne, 2003; Wallace, 2005). Thus, we might expect Nicaraguan magmas and gas emissions to be particularly HCl and H_2O-rich compared to the rest of the arc.

Further studies of volatile emissions other than SO_2 at different locations along the arc will help to elucidate some of these factors. Much further work remains to be done in order to understand the factors underpinning persistent volatile fluxes along arcs.

3.5. Comparison of subduction volatile inputs and outputs in the Central American arc

By considering other published spectroscopic measurements of the high-temperature plume at Masaya

Table 6
Electron microprobe analysis of matrix glass from fresh looking Pele's hairs (fine, brittle strands of fresh basaltic glass extruded from the lava by escaping plume gases) and volcanic bombs collected at Masaya's crater rim

Sample	Mean weight % of compound											Ref.
	SiO_2	FeO	MnO	MgO	CaO	TiO_2	Al_2O_3	K_2O	Na_2O	Cl	SO_2	
Pele's hair 2003	50.8 ± 0.2	14.9 ± 0.2	b.d.	4.9 ± 0.1	8.7 ± 0.1	1.41 ± 0.02	13.4 ± 0.1	1.42 ± 0.03	3.11 ± 0.08	0.04 ± 0.01	b.d.	a
Pele's hair 2001	50.8	13.5	0.27	4.9	9.2	1.40	13.3	1.45	2.95	0.04	b.d.	b
Bomb matrix glass 1998/1999	51.1	13.8	0.26	4.9	8.8	1.40	13.7	1.44	3.04	0.04	0.005	c
Bomb matrix glass 1981	51.7	13.0	–	4.6	8.9	1.32	13.8	1.53	2.87	0.01	0.02	d

(a) This work. Elemental compositions of glasses determined by electron probe microanalysis (WDS mode, 10 μm beam diameter, major elements: 15 kV/10 nA, trace elements: 15 kV/60 nA beam) are expressed as the equivalent weight percentage of hypothetical oxide constituents, $n = 65$. (b) Mather et al. (2003b). (c) Horrocks (2001). (d) Stoiber et al. (1986).

Table 7
Some example whole arc outputs and inputs from and to the subduction zone

Arc trench length (km)	Length of active volcanic front (km)	Output (Mg day^{-1})			Input (Mg day^{-1})		
		CO_2 degassing flux	H_2O degassing flux	HCl degassing flux	CO_2 subduction flux	H_2O subduction flux	Cl subduction flux
1450 (a)	1050 (b)	8600 (c) 6900 (d) **4400–9600** (e)	**70,000–78,000** (e)	**1300** (e)	44,000 (f) 36,000 (g) 46,000 (h)	12,000 (f) 74,000 (g) 218,000 (i)	2700 (g)

(a) The along-trench distance from the Cocos ridge to the Tehuantepec fracture zone (Plank and Langmuir, 1998). The difference between the arc trench length and the active volcanic front length reflects the complexity of the northern and southern junctions of the Caribbean and Cocos plates (e.g., Gúzman-Speziale et al., 1989; von Huene et al., 2000). (b) The distance from Tacana to Turrialba volcanoes, from Carr et al. (2003). (c) Shaw et al. (2003). (d) Hilton et al. (2002). (e) This work. (f) The contribution from structurally bound C and H in subducted sediment and igneous crust plus organic matter for C (Hilton et al., 2002). (g) The contribution from structurally bound C, H, Cl in subducted sediment and igneous crust (Jarrard, 2003). (h) From Shaw et al. (2003) which basically follows Hilton et al. (2002) but with a slightly higher input flux estimated for C from organic matter. (i) From Jarrard (2003) including pore H_2O as well.
Numbers in bold indicate new calculations from data presented here.

(Duffell et al., 2003) and the compiled 'Arc Mean' plume compositions in Gerlach (2004), we can estimate plausible mean CO_2/SO_2 and H_2O/SO_2 ratios for the Central American arc to be 1.0–2.2 and 16–18, respectively, by mass. By combining these with our new compilation of the arc SO_2 flux (Table 2), we can estimate the mean total rate that the volcanic centres along the Central American arc degas these major volatiles. The results of these calculations, as well as that for HCl (see Section 3.4), are presented in Table 7 along with other recent estimates of arc scale CO_2 degassing from Shaw et al. (2003) and Hilton et al. (2002). Shaw et al. (2003) combined new measurements of $CO_2/^3He$ with the global ^3He arc flux estimate of Hilton et al. (2002), itself derived using gas measurements and the SO_2 flux data compiled by Andres and Kasgnoc (1998), scaled to the arc length (trench length not volcanic front length). Hilton et al. (2002) calculated their arc CO_2 flux by applying a measured CO_2/S_t (where S_t is total sulphur) molar ratio to total SO_2 from the arc extrapolated from data compiled by Andres and Kasgnoc (1998). Our range of arc-scale CO_2 degassing flux brackets these previous estimates.

In Table 7, we also compare these volatile emission rates to published estimates of the inputs to the subduction-zone system from subducted material. These inputs are associated with volatiles stored in subducted components such as sediments, crust, organic matter (for C) and pore water. We have not attempted to estimate losses of volatiles from other parts of the system, whether by a return flux in the trench, or to the crust, or as stored volatiles in either erupted or intruded magma; we simply wish to make an assessment of the extent to which volcanic degassing rates might be sustained by subduction processes. Sulphur recycling is omitted from our discussion, as there are insufficient data for the Central American arc to derive an input flux, as explained above (Section 3.4).

From Table 7, it can be seen that the great uncertainty in the input flux of H_2O (e.g., the extent to which the subducted slab is serpentinised) makes it hard to assess whether this is efficiently recycled through the arc or whether the mantle is a source or sink of H_2O in subduction-related outgassing. Our estimated CO_2 and HCl fluxes suggest that in both cases the outgassing flux alone can account for a substantial component of the input flux to the subduction zone, with about 20% and 50% of the CO_2 and HCl input fluxes outgassed, respectively. Previous studies of the Izu arc (Straub and Layne, 2003) and using global data sets (e.g., Wallace, 2005) have suggested that Cl is efficiently recycled at subduction zones. The factors affecting the solubility of Cl in magmas are complex (Webster et al., 1999; Webster, 2004) but it is likely that Cl trapped in erupted or unerupted magmas (e.g., Table 6) and unerupted hydrosaline fluids may account for a substantial component of the arc output flux as well as the Cl outgassed in the plumes emanating from volcanic centres. The low solubility of CO_2 in magmas suggests that, compared to its prevalence in volcanic gas mixtures, little CO_2 is expected to be retained in erupted lavas (e.g., Blank and Brooker, 1994). Previous studies have suggested that only of order 50% of the subducted C is returned to the surface by arc magmatism, which is consistent with thermodynamic modelling showing that carbonate stability in the subducting slab and sediment may allow significant C to be transported into the deep mantle (summarised in Wallace, 2005). Our estimated return flux of CO_2 of ~25% is lower than this global average but is consistent with previous studies of the Central American arc (Shaw et al., 2003 estimated a recycling efficiency of 14–18%). It should also be noted that the degassing fluxes estimated here ignore diffuse volatile emissions (e.g., of CO_2) that are not associated with major SO_2 point sources. Extensive work is currently underway to attempt to quantify diffuse degassing rates of CO_2 from volcanoes of the Central American arc (e.g., Williams-Jones et al., 2000; Salazar et al., 2001), and completion of this work will be an essential step in properly evaluating the arc-scale volatile emissions budgets.

4. Conclusions

We present sulphur dioxide flux results from a survey in November/December 2003 of the Central American arc section from Mombacho to San Cristóbal. Individual mean fluxes were 800 Mg day^{-1} from San Cristóbal, 530 Mg day^{-1} from Telica and 220 Mg day^{-1} from Masaya. We could not resolve a flux from Momotombo. Compiling this and other data for the Central American arc suggests a mean total arc flux of ~4360 Mg day^{-1} for the period from 1997 to 2004.

Masaya volcano continues to show stable HCl/SO_2 and HF/SO_2 ratios and sustained fluxes of these components (in 2001 to 2003) of 59–65 and 5–7 Mg day^{-1}, respectively. Masaya's plume composition also appears to be stable with respect to those particulate species measured, with significant fluxes of SO_4^{2-} (4 Mg day^{-1}), Na^+ (0.9–1.3 Mg day^{-1}) and K^+ (0.7 Mg day^{-1}).

Generalising the results from Masaya to the rest of the Central American arc suggests HCl, HF and near-source sulphate fluxes of ~1300, ~170 and ~40 Mg day^{-1}, respectively, although such generalisation comes with caveats. Further, combining our arc scale mean SO_2 flux with published measurements of volcanic CO_2 and H_2O allows us to estimate mean CO_2 fluxes of 4400–9600 Mg day^{-1} and H_2O fluxes of 70,000–78,000 Mg day^{-1} for the arc. Preliminary calculations, comparing these estimates of outgassing rates with published volatile inputs fluxes into the Central American subduction zone, suggest that Cl is more efficiently recycled through the subduction zone than CO_2, which is consistent with the results of previous studies. The results for H_2O are inconclusive.

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