

The Na/Cl ratio in rainwater and the seasalt chloride cycle

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ABSTRACT

Possible seasalt and excess component sources for a variable Na/Cl ratio in rainwater have been discussed. It is shown that a separation of seasalt Na and Cl takes place during transport from sea to continent, leading to increased seasalt Na/Cl ratio (>0.86) in continental rain, which has to be regarded as the seasalt reference figure. The possible consequences for anthropogenic excess Cl deposition are discussed for the GDR. The maritime HCl degassing is assessed to be of the order of 200 kt yr^{-1} . Based on budget calculations, different Cl fluxes (emission, deposition, river run-off) have been estimated on a global scale.

1. Introduction

The interpretation of the rainwater Na/Cl ratio is based on the following formulae.

$$\left(\frac{\text{Na}}{\text{Cl}}\right)_{\text{sample}} = \frac{\left(\frac{\text{Na}}{\text{Cl}}\right)_{\text{sea}} \left[1 + \frac{\text{Na}_{\text{ex}}}{\text{Na}_{\text{sea}}}\right]}{1 + \frac{\text{Cl}_{\text{ex}}}{\text{Cl}_{\text{sea}}}}, \quad (1)$$

Na and Cl denoting the concentrations of sodium and chloride, respectively. By neglect of any excess sodium contribution (mainly soil-derived), there results from eq. (1) a simple equation to estimate the excess chloride concentration in rainwater samples (in this case $\text{Na}_{\text{sample}} = \text{Na}_{\text{sea}}$):

$$\text{Cl}_{\text{ex}} = \text{Cl}_{\text{sea}} \left(\frac{R_{\text{sea}}}{R} - 1\right) = \text{Cl}_{\text{sample}} - \frac{\text{Na}_{\text{sample}}}{R_{\text{sea}}}, \quad (2)$$

where $R = \text{Na/Cl}$ for the sample. By analogy, we get for the estimate of excess sodium, neglecting any excess chloride (mainly man-made),

$$\text{Na}_{\text{ex}} = \text{Na}_{\text{sample}} - R_{\text{sea}} \text{Cl}_{\text{sample}}. \quad (3)$$

For the ratio R_{sea} generally, the value R_{bulk} for seawater is used (0.56 or 0.86 as mass or molar ratio; in this paper, only molar ratios are used). R_{bulk} varies by less than 2% for different oceans and locations (Sea Water, 1972).

The estimate of excess Cl in polluted areas is important for assessing the fate of man-made HCl emissions (Lightowers and Cape, 1988). The question pivots, however, on the value of the reference ratio R_{sea} . The aim of this paper is to show that the relation $R_{\text{sea}} = R_{\text{bulk}} = 0.86$ is not appropriate for rainwater above land; a hypothesis of separation of Na and Cl during the transport from sea to continent is made, together with an assessment of the chloride fluxes, which results in $R_{\text{sea}} > 0.86$. Some factors influencing the Na/Cl ratio and excess Cl deposition over land will be discussed.

2. Separation of Na and Cl during the transport from sea to continent

There is no indication that a separation takes place during the seasalt production at the sea-air interface (Blanchard, 1983; Weisel et al., 1984). At first, Junge (1956) showed a Cl loss in fine marine aerosol particles. Eriksson (1960) has proposed that Cl loss occurs as a consequence of pH-lowering reactions between seasalt particles and other atmospheric constituents. Many studies deal experimentally and theoretically with the estimation of Cl loss in marine aerosols due to the

Table 1. Estimated residence times τ , dry deposition velocity v_d and mixing height h of different marine Cl species

Form	Wet deposition τ_w (days)	Mixing height* h (m)	Dry deposition		Total τ (h)
			v_d (cm s ⁻¹)	τ_d (h)	
coarse particles	} ~2.5 [†]	30	4.5–6 [‡]	0.1–0.2	0.1–0.2
fine particles		1500	~1 [§]	~42	~25
gaseous HCl		1000	~2 [¶]	~14	~11

* To be assumed based on published profiles (Gordon et al., 1977; Blanchard et al., 1984).

[†] Roughly estimated, based on a continental mean of 4 d (Möller, 1982).

[‡] Corresponding to wind speeds of 8–10 m s⁻¹ (McDonald et al., 1982) as well as 15–20 $\mu\text{g m}^{-3}$ seasalt concentration (Erickson et al., 1986).

[§] Sievering (1984).

[¶] Dollard et al. (1987); other investigators (Kritz and Rancher, 1980; Cocks and McElroy, 1984) assumed 0.8 cm s⁻¹, whereas Lightowlers and Cape (1988) pointed out that v_d may be higher than 0.8.

$R > 0.86$ if there are no excess contributions (Fig. 1). At first, Jacob et al. (1985) gave a similar explanation for their results of $R > 0.86$ in fogwater at the Californian coast.

3. The chloride fluxes

3.1. Global chloride cycle

Based on the numbers presented in Table 1, it is possible to assess the atmospheric mass $M = \bar{c}h$ (h mixing height) and the flux $F = M/\tau$ (see Table 2). Neglecting all rather high uncertainties of the data (\bar{c} , h , v_d) based only on a few experiments, the assessed HCl flux corresponds to 30–60% of HCl degassing from fine aerosol, which is in the probable range experimentally found (see Section 2); Yue et al. (1976) estimated theoretically the possible range of HCl loss between 173–932 Tg yr⁻¹. There results from Table 2 a total seasalt flux (in term of emission) of about $1 \cdot 10^{10}$ t yr⁻¹ (corresponding to around $5.5 \cdot 10^9$ t yr⁻¹ Cl flux). This estimate agrees with the upper figure of the maritime seasalt deposition of $(5-10) \cdot 10^9$ t yr⁻¹ based on the earlier estimated seasalt sulphate deposition of 120–250 Tg S yr⁻¹ (Várhelyi and Gravenhorst, 1983; Mészáros, 1982; Möller, 1983).

Galloway et al. (1983), by using a shipboard wet-only collector above the Atlantic found a mean Cl concentration of 5.3 ± 4.0 mg l⁻¹ (Table

3). Accepting this value as a global average, taking into account the total yearly maritime rainfall ($412 \cdot 10^{15}$ l after Barney, 1980), a Cl wet deposition of 2200 ± 1700 Tg yr⁻¹ follows. From the data listed in Tables 1 and 2, however, the wet deposition flux according to $F_w = M/\tau_w$ can be estimated as being in the range of 200–300 Tg yr⁻¹, corresponding to a mean Cl concentration in rain of 0.5–0.8 mg l⁻¹.

This discrepancy may be a result of the strong influence of dry deposited seasalt to the rainwater sample. Assuming an annual rainfall contribution of 10% to the year, the dry deposited Cl amounts to around 550 Tg yr⁻¹ during this time period, i.e., the “wet only” deposition should be 750–850 Tg yr⁻¹. Re-arranging the data of Galloway et al. (1983) into a group A of low seasalt concentrations (corresponding to low wind speeds and consequently minor dry deposition; unfortunately, wind speeds are not given in this paper) and a group B for high concentrations (Table 3), there results a “wet only” Cl deposition of 700 ± 125 Tg yr⁻¹, in good agreement with the above estimate (equivalent to 1.7 ± 0.3 mg l⁻¹).

The total maritime Cl deposition and seasalt emission remains uncertain. Blanchard (1985) summarized his discussion that “we can do no better than say that the global seasalt production is probably between 10^9 and 10^{10} t yr⁻¹”. However, most of the more recent indications tend to the upper limit.

Table 2. Estimation of seasalt and maritime Cl fluxes

	\bar{c} ($\mu\text{g m}^{-3}$)	M^\S ($\mu\text{g m}^{-2}$)	F ($\text{g m}^{-2} \text{ yr}^{-1}$)	F^\P (Mt yr^{-1})	F_{Cl} (Mt yr^{-1})
coarse seasalt	15–20*	0.45–0.60	~28	~9000	5000 [¶]
fine aerosol	5 [†]	7.5	~2.6	~900	300–400
gaseous HCl	0.08–0.16 [‡]	0.8–1.6	0.6–1.3	200–400	200–400

* Erickson et al. (1986), cf. Table 1.

[†] Estimated from profiles of Blanchard et al. (1984).

[‡] Vierkorn-Rudolf et al. (1984).

[§] Column concentration (mg m^{-2}) over the Biskaya, 7.5 for particulate Cl and 1.3 for gaseous HCl (Fuchs et al., 1985).

[¶] Assuming a not ice-covered world ocean area of $3.3 \cdot 10^{14} \text{ m}^2$ (Blanchard, 1985); the total seasalt flux ($10^{10} \text{ t yr}^{-1}$) agrees with Blanchard's estimate.

^{||} Assuming $R = 0.86$, i.e., no Cl loss.

^{|||} Assessed as budget difference from HCl degassed fine seasalt and gaseous HCl.

Table 3. Mean rainwater composition and standard deviation ($\mu\text{eq l}^{-1}$) above the Atlantic (after Galloway et al., 1983) and maritime wet deposition (Tg yr^{-1})

	n	Cl	Na	Na/Cl	H^+	Δ^\ddagger	$\text{SO}_4^{2-}(\text{ex})^\S$
all samples	19*	148 ± 114	131 ± 102	0.91 ± 0.08	13.7 ± 10.6	10.1	10.4 ± 9.0
group A	9	49 ± 9	46 ± 7	0.96 ± 0.06	17.3 ± 10.7	14.0	12.4 ± 6.6
group B	10 [†]	236 ± 89	206 ± 87	0.86 ± 0.06	10.4 ± 9.3	5.4	8.4 ± 10.4
deposition [†]		700 ± 125	450 ± 80	—	7 ± 4	—	70 ± 60

* Without sample No. 0 5 (Na/Cl = 0.46) in Galloway et al.

[†] Based on group A; sulphate based on all samples.

[‡] $\Delta = \text{H}^+ - (c_A - c_B)$, where $c_A = \text{Cl} + \text{SO}_4^{2-} + \text{NO}_3^-$ and $c_B = \text{Na} + \text{Mg} + \text{Ca} + \text{K} + \text{NH}_4^+$.

[§] $\text{SO}_4^{2-}(\text{ex}) = \text{SO}_4^{2-}(\text{sample}) - \text{SO}_4^{2-}(\text{sea})$, where seasalt sulphate is based on Na to be assumed as seasalt only.

It is generally accepted (Eriksson, 1960; Granat et al., 1976; Blanchard, 1985) that 10% of the seasalt production falls on land. The typical inland rainwater Cl concentrations at remote sites on different continents seems to be in the range 0.5–0.9 mg l^{-1} (Söderlund and Granat, 1982; Johnson, 1981; Zhao and Sun, 1984). For the Cl wet deposition, we get 50–90 Tg yr^{-1} (global land rainfall $104 \cdot 10^{15} \text{ l yr}^{-1}$)*.

The global river run-off has been estimated to be 230–260 Tg yr^{-1} using Cl concentrations in river water between 6.4 and 7.9 mg l^{-1} (Alekin,

1970; Berner, 1971). Human salt production contributes to this flux, especially due to fertilizer production and application. According to Eriksson (1960), the Cl weathering is negligible. The seasalt run-off could be in the order of 200 Tg Cl yr^{-1} , removing the salt pollution.

In Fig. 1, the global seasalt Cl cycle is presented in a simplified way by summarizing the figures referred to. The most interesting findings are:

(i) the maritime dry to wet deposition ratio seems to be around 10;

(ii) the continental dry to wet deposition ratio of seasalt Cl is of the order of 2;

(iii) the ocean to land seasalt transport amounts $\approx 5\%$ of the seasalt emission.

Based on the fluxes assessed, it is possible to

* In the global Cl cycling, we can neglect all atmospheric excess contributions (man-made, volcanic, CH_3Cl photochemistry) which amount to around 6–15 Tg yr^{-1} (see data in Legrand and Delmas (1988)).

estimate the Na/Cl ratios: 1.2–2.2 for fine maritime aerosol (corresponding to 30–60% Cl loss), 0.9–1.5 for “pure” maritime rainwater and 0.87–1.10 for wet only sampled rainwater; bulk samples, however, correspond to ~ 0.86 (all figures valid only for long time averages). These estimates are in excellent agreement with the experimental findings of Galloway et al. (Table 3). Na/Cl for wet only sampled rainwater (all samples) amounts to 0.91; the ratio is higher (0.96) for nearly “pure” rain (group A) and amounts to 0.86 for samples influenced strongly by dry deposition (group B).

The ocean to continent Cl transportation within cloud water ($33 \cdot 10^{15}$ l yr⁻¹) is less than 10% of the aerosol transport. The resulting seasalt reference ratio for land rainwater is therefore $R_{\text{sea}} = 1.1$ –1.8. For single events, however, this ratio can vary, depending on the life history of rain clouds and the relation between in-cloud and sub-cloud scavenging.

3.2. HCl flux assessment based on acid budget estimate

The HCl flux of 200–400 Tg yr⁻¹ that has been estimated in Subsection 3.1 on the basis of cycle calculation must be stoichiometrically balanced by H⁺. According to eq. (4), we have to supply 5.5–11 Teq H⁺ through related anions (HSO₄⁻, NO₃⁻) as well. From recently established global acid budget assessment (Möller and Horváth, 1988), the following H₂SO₄ and HNO₃ burden in the marine atmosphere should be valid:

$$F(\text{H}_2\text{SO}_4) \approx 0.3Q(\text{DMS}) + 0.6Q(\text{SO}_2\text{-volc} + \text{CS}_2 + \text{COS}) \approx 18 \text{ Tg S yr}^{-1} \\ \approx 1.1 \text{ Teq H}^+ \text{ yr}^{-1},$$

$$F(\text{HNO}_3) \approx 1.0Q(\text{NO}) \approx 5 \text{ Tg N yr}^{-1} \\ \approx 0.4 \text{ Teq H}^+ \text{ yr}^{-1}.$$

The maximum naturally produced acidity amounts to about 1.5 Teq H⁺ yr⁻¹, which is considerably less than needed for the assessed HCl flux. A possible anthropogenic H₂SO₄ contribution to the marine atmosphere (10–25 Tg S yr⁻¹ according to Möller, 1983) might increase this figure. However, this sulphate (besides anthropogenic NO₃⁻) is probably neutralized (Möller and Zierath, 1986) through man-made and soil-derived alkaline components (NH₄⁺, Ca²⁺, K⁺).

The following questions should be put in order to solve this contradiction.

(1) Is the total HCl loss smaller (by a factor of 2–4)?

(2) Is the marine DMS emission and/or NO production higher than known?

(3) Is the global annual volcanic SO₂ emission higher (assumed to be only 2 Tg S yr⁻¹ in this estimate)?

(4) Might the needed H⁺ be given by unknown acids?

The importance of organic acids for contribution to free acidity in rainwater in remote areas is pointed out by Galloway et al. (1982). However, these weak acids ($K_{\text{HX}} \ll 1$) seem to be unlikely to displace HCl significantly (Brimblecombe and Clegg, 1988).

4. The continental Na/Cl ratio

Due to local Na and Cl sources (see Fig. 1), the resulting rainwater Na/Cl might vary ($\cong 0.86$). In this section, a data analysis will be given from the European Air Chemistry Network (EACN) and other precipitation chemistry data (Table 4) to support the hypothesis of $R_{\text{sea}} > R_{\text{bulk}} = 0.86$ for continental rainwater, with some indications of excess sodium and chloride contributions as well.

The average Na/Cl ratio from 42 Scandinavian inland stations (nos. 3 and 7 in Table 4) amounts to 1.16 ± 0.33 (mean Cl = 24 $\mu\text{eq l}^{-1}$). Assuming no excess Cl (negligible HCl emission, see Table 4) and negligible soil Na (small enrichment factors, see Table 6), this figure might represent the reference ratio R_{sea} , which has been derived as being between 1.1 and 1.8 (cf. Fig. 1). In contrast to that, Na/Cl amounts to 0.90 ± 0.05 for high maritime influenced sites (mean of nos. 1, 4, 6, 9, 10 in Table 4; $n = 30$, Cl = 244 $\mu\text{eq l}^{-1}$), a typical figure, as to be expected for maritime rainwater (cf. Fig. 1).

At some locations, however, the Na/Cl ratio is significantly less than 0.86 (GDR, Czechoslovakia, Austria; see Table 4), caused probably by man-made HCl emission. It is interesting to note that despite low HCl emission in Austria, the rainwater is characterized by high excess Cl, most likely caused from neighbouring countries.

More information is available from precipitation chemistry data based on a subdivision into

Table 4. Rainwater composition ($\mu\text{eq l}^{-1}$) and Na/Cl ratios from the EACN (monthly bulk sampling; Söderlund and Granat, 1981, 1982) and other locations (arithmetic means)

No.	Location	Number of stations	Na	Cl	Na/Cl	Man-made HCl emission $\text{g m}^{-2} \text{yr}^{-1}$
1	Sweden	4	278 ± 185	289 ± 199	0.96 ± 0.10	
2	Sweden	8	64 ± 12	65 ± 14	0.99 ± 0.15	0.02*
3	Sweden	35	29 ± 14	24 ± 10	1.17 ± 0.36	
4	Norway	5	177 ± 203	293 ± 248	0.86 ± 0.03	
5	Norway	7	26 ± 9	23 ± 8	1.12 ± 0.17	0.006*
6	Iceland	2	207 ± 66	246 ± 57	0.82 ± 0.08	
7	Ireland	9	503 ± 297	523 ± 331	1.00 ± 0.07	negl.
8	UK	10	478 ± 439	468 ± 489	1.19 ± 0.29	1.07*
9	Denmark	15	188 ± 55	209 ± 69	0.91 ± 0.04	0.23*
10	Netherlands	4	240 ± 213	266 ± 236	0.90 ± 0.06	0.49*
11	Belgium	4	66 ± 28	81 ± 34	0.81 ± 0.04	0.67*
12	France	5	44 ± 18	54 ± 19	0.79 ± 0.08	0.20*
13	GDR†	11	47 ± 11	92 ± 30	0.53 ± 0.10	0.88‡
14	Czechoslovakia‡	1	7 ± 4	13 ± 9	0.50	0.76§
15	Austria	4	14 ± 2	26 ± 8	0.58 ± 0.14	0.02*
16	Hungary¶	6	24 ± 6	29 ± 3	0.83 ± 0.20	
17	Hungary¶	8	65	38	1.65	0.10§

* According to Lightowers and Cape (1988).

† Unpublished data.

‡ Background station in Bohemia, wet only (1976–84); Moldan et al. (1987).

§ Assessed from coal combustion using emission factors of 1.4 kg t^{-1} hard coal and 0.3 kg t^{-1} lignite.

¶ Wet only sampling 1977–80 (Horváth, 1981).

|| Bulk sampling 1968–70 (Horváth and Mészáros, 1984).

Table 5. Sector analysis of precipitation-weighted rainwater composition ($\mu\text{eq l}^{-1}$) in the GDR (G—Greifswald, S—Seehausen)*, n number of samples

Sector (degrees)	337–36 (S) 320–33 (G)	37–105	106–208	209–259 (S) 209–248 (G)	260–295 (S) 249–279 (G)	296–336 (S) 280–319 (G)	0–360
Characteristic	“Baltic Sea”	“Eastern”	“GDR”	“FRG”	“Northwestern”	“North Sea”	All†
n (S)	39	35	109	168	182	104	712
n (G)	46	13	67	76	105	72	434
Cl (S)	64	55	89	68	59	129	66 (87)
Cl (G)	82	20	66	33	52	139	61 (94)
Na (S)	28	16	32	26	30	87	31 (45)
Na (G)	55	10	24	13	27	108	36 (59)
Na/Cl (S)	0.44	0.29	0.36	0.38	0.51	0.67	0.47
Na/Cl (G)	0.67	0.50	0.36	0.39	0.52	0.78	0.58

* Stations of the Meteorological Service of the GDR; wet only event sampling since 1982 (S) and 1984 (G); data from Marquardt (personal communication, 1988).

† In parenthesis, arithmetic means.

Table 6. *Enrichment factors (bulk to wet only sample concentration ratio) for Na and Cl*

	A	B	C	D	E	F
Na	1.14	1.16	1.44	3.92	1.50	2.78
Cl	1.11	1.12	1.06	1.92	1.36	1.40

A: Monthly average from 5 inland background stations in Sweden (Granat, 1987).

B: Coastal site in the Netherlands, mean of 16 collectors (Asman and Slanina, 1980).

C: Coastal site at Bodden (Greifswald) in the GDR, weekly sampling (Marquardt, personal communication, 1988).

D: Rural site in the Altmark (Seehausen) in the GDR, weekly sampling (Marquardt, personal communication, 1988).

E: Rural background station in Central Bohemia (Czechoslovakia), monthly sampling (Moldan et al., 1987).

F: Average from 7 background station in Hungary, not simultaneous (Horváth and Mészáros, 1984).

characteristic sectors of rain cloud history (Table 5). One can see that the lowest Na/Cl (highest excess Cl) comes from polluted areas in the GDR and FRG ($\bar{R} = 0.37$), which represent 41% of all events. On the other hand, the Na concentration in samples from the sector "GDR" is significantly higher than that from both neighbouring sectors (Table 5) which can only be explained by a sodium excess contribution, most likely as soil dust, however, a contribution from flue ash emission cannot be excluded. The high enrichment factors (Table 6) for Na (especially in contrast to Cl) are an indication of particulate Na deposition. An extreme example for excess Na from soil dust seems to be Hungary (cf. Tables 4 and 6).

The consequences for calculating the excess Cl percentage in rainwater for the GDR are as follows. Based on $R_{\text{bulk}} = 0.86$, the excess Cl can be calculated to be 38%, but using the new value $R_{\text{sea}} = 1.16$, it increases to 54%. To continue this example, assuming a portion of 30% excess Na (based on $\sim 10 \mu\text{eq Na l}^{-1}$ derived from Table 5) compared to the total Na (Table 4), the excess Cl increases up to 65%. On the basis of around 125 kt yr⁻¹ total Cl wet deposition in the GDR (Möller, unpublished), the corresponding excess Cl depositions are 50, 70 and 80 kt yr⁻¹, respectively. Furthermore, we have to take into account

the HCl dry deposition, which has been assessed only with high uncertainty in the order of 30 kt yr⁻¹ (based on $0.5 \mu\text{g m}^{-3}$ as mean HCl concentration). In this way, the excess Cl deposition seems to be of the order of the anthropogenic HCl emission in the GDR, estimated to be around 90 kt yr⁻¹ (Möller, unpublished). However, accepting the higher figures based on corrected seasalt Cl and excess Na, the excess Cl deposition might exceed the emission.

The problem may be more complicated, because the derived $R_{\text{sea}} = 1.16$ could change within different regions of the continent due to climatic conditions and the possible further reaction (4) with acidifying components of anthropogenic origin. The $R_{\text{sea}} = 1.16$ is possibly only valid for Northern Europe. However, a further HCl loss in the continental atmosphere is not so likely, because (a) an essential portion of anthropogenic acids (SO_x , NO_x) is neutralized by alkaline matter (NH_3 , Ca, Mg), see Möller and Zierath (1986), (b) owing to man-made HCl emissions, linked in general with the major emissions of SO_2 and NO, the existing atmospheric HCl partial pressure does not favour a HCl loss from the already highly Cl depleted NaCl aerosol.

5. Conclusions

Despite all uncertainties of assumptions and data used in this paper, the following conclusions can be drawn, where the quantitative figures, of course, have to be regarded with caution.

(1) Due to the separation of seasalt Na and Cl, the Na/Cl ratio could be 1.2–2.2 for fine marine aerosol, ≥ 0.9 for maritime rainwater wet only sampled, ~ 0.86 for bulk maritime rainwater and 1.1–1.8 for continental rain, not influenced by excess Na and Cl.

(2) Maritime rainwater, wet only collected below altitudes of 30 m is influenced by dry deposited seasalt (dry/wet ≈ 4).

(3) The maritime HCl degassing is likely to be of the order of 200 kt yr⁻¹, where the anorganic acids H_2SO_4 and HNO_3 produced from natural emitted S- and N-compounds contribute only up to 30% and the remaining needed proton source is unknown.

(4) The ratio of dry to wet Cl deposition has been estimated to be 10 for the oceans and to be 2 for continents.

(5) The seasalt production seems to be around 10^{10} t yr⁻¹, which is at the upper limit of earlier estimations.

(6) The excess Cl deposition in the GDR is at least as high as the GDR man-made HCl emission.

To reduce the uncertainties, it should be recommended that more experimental data are required on Na/Cl ratios in seasalt aerosols as regards dependence on particle size, measurements of gaseous HCl and of Na and Cl in

continental aerosols to assess the possible source strength of soil dust. The evaluation of a reference ratio R_{sea} is very important for estimating the excess Cl deposition and therefore the fate of man-made HCl.

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