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Long-term seismotectonic influence on the hydrochemical composition of a spring located at Koryaksky-Volcano, Kamchatka: deduced from aggregated earthquake information

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Abstract The analysis of earthquake-related signals in hydrochemical time series is still a challenging task. Mostly it is unclear how the geometrical and energetic distribution of earthquakes is influencing variation in the hydrochemical composition of monitoring sites, e.g. located close to volcanoes. Past research showed that linear stress-release models alone are not capable to explain sufficiently observed variation in hydrochemical time series due to earthquake activity. A spring located at the base of Koryaksky Volcano, which has shown hydrochemical variation close to 5, major earthquakes, was chosen to analyse relation patterns between hydrochemical variation and seismicity. A possible mechanism, explaining observed hydrochemical variation, that seismic waves trigger an underground water pumping caused by nucleation of gas bubbles in magma was proposed. Consequences are an increase of discharge, gas content in water and changes in the mixing ratios of waters of different genesis. Based on functions of aggregated earthquake information (E) it is herein shown that seismotectonic-triggered processes have a significant influence on the variation of the hydrochemistry of the spring, lasting longer than two decades. At least seven categories of relation patterns between hydrochemical variation and seismotectonic activity E can be identified. A conducted spectral analysis shows that earthquake activity and hydrochemistry share spikes in frequencies. Results prove that the use of functions of transformed aggregated seismic observations is useful to represent the seismotectonic activity for analysing earthquake-related signals in hydrochemical time series.

Keywords Earthquake · Volcano · Hydrochemistry · Seismotectonics · Aggregation function · Kamchatka

Introduction

In the past decades, hundreds of observed potential earthquake-related signals in hydrochemical or gasgeochemical monitoring time series were reported. A summary of these findings can be found in, e.g. Toutain and Baubron (1999) or Hartmann and Levy (2005). Only a few studies report clear single signals preceding an earthquake (e.g. Toutain et al. 1997). Coseismic and postseismic signals in hydrological and hydrochemical monitoring time series are more often reported and mostly more clear (e.g. Zongjin 1990; Igarashi and Wakita 1995; Tsunogei and Wakita 1995; Silver and Wakita 1996; Bella et al. 1998; Hartmann 2005). Long time series can help to identify which seismotectonic patterns are inducing variation in a hydrochemical monitoring time series to extract site-specific patterns (Hartmann 2005).

Explanation for earthquake-related signals

A significant change in the hydrochemical composition of a monitored site can be the result of the mixing of aquifers containing waters of different genesis (e.g. Hartmann et al. 2005). This effect is known as mixing aquifers. A well-documented example of mixing aquifers related to seismotectonic processes on Vulcano Island, Italy, is given in Bolognesi (1997). Altered aquifer conditions resulting in changed mixing ratios of waters with different genetic origin is one proposed mechanism for the observation of earthquake-related signals. Several models are proposed in the literature to explain these observations: (a) static stress release by single earthquakes (e.g. Dobrovolsky et al. 1979), (b) viscoelastic relaxation of the earth's crust (e.g. Hill et al. 2002) and (c) dynamic triggering (e.g. Gomberg et al. 1998). However, those models are discussed controversially in the literature (Hill et al. 2002). Nevertheless, earthquake-related hydrological and hydrochemical signals

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can be observed up to 1,000 km away from the epicentre of single major earthquakes (e.g. Roeloffs 1996; Igarashi and Wakita 1995). Static stress release models, based on the assumption of a homogeneous underground and focusing only on single large earthquakes, are not sufficient to explain all reported earthquake-related signals or significant variations in monitoring time series.

Hill et al. (2002) point out that earthquakes are capable of triggering volcanic eruptions. Those earthquakes may lead to a relaxing magma body, sinking crystal plumes, hydraulic surge or advective overpressure and rectified diffusion before eruption (Hill et al. 1993; Mangan and Sisson 1996). In addition, Linde and Sacks (1998) show that there are significantly more eruptions immediately following large earthquakes (including distant ones) than before.

If the proposed processes are capable of triggering eruptions, they should also be capable of triggering changes in the earth's crust or magma chambers, not necessarily leading to eruptions but changing aquifer conditions. To identify long-lasting seismotectonic influences on hydrochemical time series related to changes in aquifer conditions, a long hydrochemical time series is essential.

Problems in identifying earthquake-related signals

Traditionally the “one earthquake–one signal” approach is used to identify signals in hydrochemical or gasgeochemical monitoring time series. The research for earthquake-related signals is focusing on signals related to large seismic events. This approach neglects the possibility that seismotectonic processes resulting in small seismic events instead of single major seismic events may have in addition a direct or indirect effect on the composition of the hydrochemistry of the water or that regional tectonic processes can have a continuous influence on the water composition. The research for seismotectonic-induced variation in monitoring time series should include information of all available seismotectonic events to identify even the not so obvious relations between earthquakes and volcanoes, and variation in hydrochemical monitoring parameters.

Why aggregating earthquake information?

Analysis of earthquake-related signals with the “one earthquake–one signal” method is difficult, if local mechanisms leading to earthquake-related signals are unknown and hydrochemical/gasgeochemical time series show high variation with time. General rules or models for detecting whether one earthquake or an earthquake cluster correlates to an apparent identified signal are still not established (Hartmann and Levy 2005; Hartmann et al. 2005). Observed signals, which seem to have a clear precursory relation to an earthquake, are rare (Hartmann and Levy 2005). Examples

of clear hydrochemical signals supposed to be related to single earthquakes are given in, e.g. Tsunogai and Wakita (1995), Silver and Wakita (1996) or Zongjin (1990). Changes in monitoring time series of wells or springs caused by seismotectonic activity and related to (a cluster of) small earthquakes are seldom documented in detail but exist, e.g. Bolognesi (1997). To overcome the problem of excluding relevant information, the aggregate earthquake information can be an appropriate method (Hartmann 2005). It was shown that with the technique of aggregating seismotectonic information more earthquake-related variations in a gasgeochemical monitoring time series can be identified than using information from a single major earthquake.

Former findings deduced from hydrochemical time series analysis in Kamchatka

For analysing the long-term relation patterns between seismotectonics and a hydrochemical time series, published data from a spring (Fig. 1) located at Koryakski Volcano, Kamchatka, were chosen in this study (Bella et al. 1998). The time series showed to five major earthquakes a significant postseismic variation in discharge and hydrochemistry. Biagi et al. (2003) proposed that seismic waves trigger underground water pumping underneath the spring caused by nucleation of gas bubbles. This resulted in an increase of discharge and gas exhalation accompanied by significant hydrochemical variation. In the area of Petropavlovsk, Kamchatka several springs and monitoring wells are probed for more than 20 years by the Geochemical Laboratory of the Geophysical Service of Kamchatka (Kopylova et al. 1994; Bella et al. 1998; Biagi et al. 2003).

They are located near the subduction zone in Kamchatka and are close to the Koryaksky Volcano. In this subduction zone stress is continuously built up due to the subduction process and released, resulting in seismic activity.

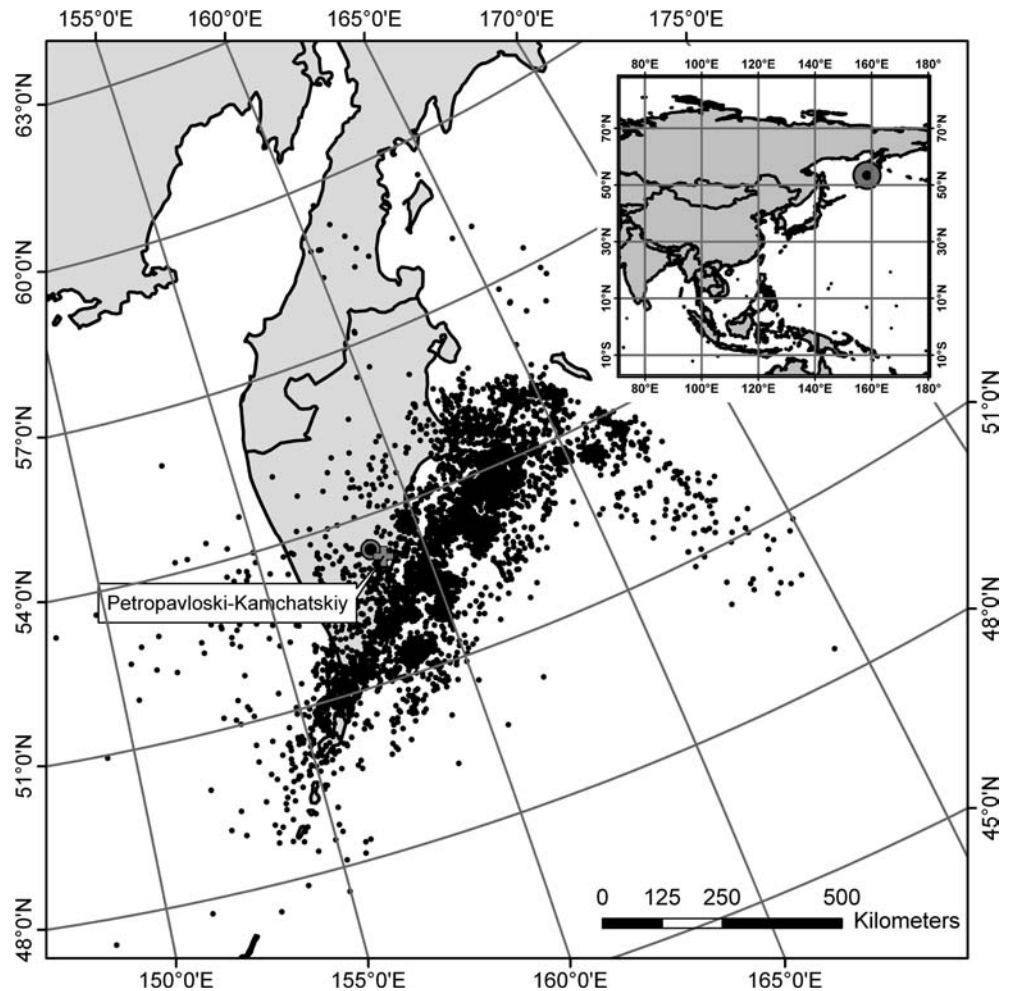
Various studies on these sampled springs and wells have shown that processes related to large earthquakes ($M > 6.0$ and distance < 250 km) have a significant influence on the composition of their hydrochemistry (e.g. Khatkevich 1994; Kopylova et al. 1994; Bella et al. 1998; Biagi et al. 2000a–c). Those works identified for three major earthquakes potential precursory and to five major earthquakes co-/postseismic variation in the hydrochemistry of several wells.

The monitoring site

Earthquake information

Data used within this study and information about the used earthquake catalogue was published in Bella et al.

Fig. 1 Location of the spring located at Koryaksky Volcano. The map shows the distribution of 5,487 earthquakes used in this study and occurring between January 1977 and December 1998



(1998) and Biagi et al. (2000a, b). The available earthquake catalogue contains 5,487 earthquakes with events of magnitude larger than 4 within the analysed period. The original data sampling was conducted by the Hydrogeoseismic Group of the Geophysical Service in Petropavlovsk.

The Peninsula Kamchatka contains more than 80 volcanoes with an underlying subduction zone. The region is characterised by strong earthquake activity (Fig. 1), whereby the majority of earthquakes occur in a zone located 60–100 km offshore (Kopylova 1994; Biagi et al. 2003). Hypocentral depths reach until 650 km and the depth of the earthquakes are, in general, dependent on their relation to the subduction zone. The analysis of the earthquake catalogue reveals that earthquakes in the continental part of Kamchatka occur less frequently. This seismic activity is mostly related to volcanic activity with magnitudes rarely exceeding 6 and with focal depth less than 50 km (Gordeev et al. 1998).

Regional seismic activity is characterised by periods without strong earthquakes ($M > 6$, epicentral distance less than 250 km). In the period from 1977 to 1986 no earthquake with magnitude larger than 6 and closer than 250 km to the monitoring site was observed, whereas in

the period from 1986 to 1998 several earthquakes with magnitude larger than 6 occurred (Kopylova 1994; Bella et al. 1998). In this study, all 5,487 earthquakes with magnitude larger than 4 and an epicentral distance less than 1,000 km from the spring-site are included. The analysed time span lasts 7,500 days, starting from the 1 January 1977.

Hydrochemical information

The coordinates of the herein analysed spring (identical with spring 1 in Bella et al. 1998) are $53^{\circ}23.6' N$ and $158^{\circ}25.4' E$. The spring was sampled with a mean sampling frequency of 3 days since January 1977, measuring flow rate, temperature, ion content (Cl^{-} , HCO_3^{-} , SO_4^{2-} , Na^{+} , K^{+} , Li^{+} , Ca^{2+} , Mg^{2+} , H_3BO_3 , H_4SiO_4 , all in mg/l) and dissolved gases (O_2 , N_2 , Ar, CO_2 , H_2 , CH_4 , He, in ml/l). Gases were measured since 1984. An overview of the data characteristics is given in Table 1. The measurement values are linearly interpolated on a daily basis. The spring is located at the foot of the Koryaksky Volcano at the location “Pinachevo” near the Petropavlovsk fault, which is separating the volcano

Table 1 Characteristics of the hydrochemical data (1984–1998)

	Mean	Median	Minimum	Maximum	Variance
<i>Q</i>	0.31	0.33	0.10	1.09	0.02
PH	7.30	7.30	7.00	8.15	0.01
Temperature	6.91	6.87	5.50	8.50	0.22
Cl ⁻	126.26	111.30	60.30	333.30	2,174.60
H ₃ BO ₃	10.82	9.73	4.10	25.80	11.67
HCO ₃ ⁻	117.12	111.80	84.20	219.60	454.03
Na ⁺	86.97	80.17	44.80	195.50	654.27
Ca ²⁺	11.51	10.40	5.60	30.50	14.07
H ₄ SiO ₄	66.94	66.70	61.00	73.70	2.27
K ⁺	4.51	4.40	3.44	8.67	0.53
Mg ²⁺	9.82	8.80	7.30	25.50	9.06
Ar	43.30	43.27	6.39	103.00	18.50
CO ₂	9.98	9.60	2.90	26.40	8.02
Gas pressure	32.99	32.27	21.60	98.10	18.54
H ₂	20.50	5.50	0.10	2,327.10	5,766.61
N ₂	19.49	19.33	7.20	73.90	6.34
O ₂	1.53	1.50	0.10	14.60	0.88
CH ₄	154.22	53.65	0.07	1,495.00	67,351.08

chain of East-Kamchatka from the Malka-Petrovsk-fault zone.

The spring water is a mixing of highly mineralised deep water represented in a well (Gk-1 in Kopylova 1994) located close to the spring and less mineralised, surface near ground water. The mineralisation compound is on average 0.43 g/l and from the type HCO₃-Cl-Na. The waters at the location are nitritic-methane thermal waters.

To figure out which components of the measured variables should be analysed a factor analysis focussing on the dissolved ions was carried out (Table 2). A second factor analysis (1984–1998) was carried out including gases, because they were first measured in 1984 (Table 3). Components explaining the factor 1 with more than 53 and 38%, respectively, of the total variance (Tables 2, 3) fit with the interpretation that the spring water chemistry is a mixing of the higher mineralised deeper water similar to the well GK-1 (9.1 g/l) and the ground water from shallow aquifers (Kopylova et al. 1994). The variable methane is coinciding with factor 1, correlating highly with the major dissolved ions. This strengthens the interpretation that one end-member is related to the deeper highly mineralised ground water. All factors together very well declare the total variance as the communalities show (Tables 2, 3). The parameter discharge shows a high correlation with both extracted factors in Table 2. From this it can be concluded that factors controlling the contribution of deeper waters to the spring water chemistry are influencing only partly the variation in discharge. Figure 2 gives an overview of the parameters discharge, chloride and methane concentration. High amplitudes in all three time series coincide in the time period between days 3,800 and 7,000. Former studies focusing on the earthquake-related variation in hydrochemistry in the considered region showed that chloride is a parameter with a clear relation to major earthquakes (Bella et al. 1998;

Biagi et al. 2003). Chloride is a good parameter for investigation as it is conservative and does not change abruptly. Hydrochemical parameters grouping on factor 2 in Table 2 show lower variation due to major earthquakes. Hence chloride was chosen here for further investigation.

Methodology and analysis

Aggregation of earthquake information

There exist two central problems when analysing the connection between a time series, which describes the occurrence and amplitude of earthquakes, and a hydrochemical time series:

1. The earthquake time series is not univariate, but it is composed of at least four independent variables, with one expressing the released seismic energy and three specifying the spatial (three-dimensional) coordinates of the hypocenter.
2. Earthquakes occur at irregular time intervals and in most cases are not synchronous with the time of sampling of the spring water. Bolognesi (1997) showed that changes in the chemical composition of the water in a well due to a seismotectonically induced change in the mixing ratio of waters of different origin are not necessarily related to a single earthquake, but may represent the hydrochemical response to a sequence of seismo-tectonic events, occurring over a period of time.

Consequently, in order to investigate the interdependency between seismicity and hydrochemical monitoring time series the earthquake time series has to be transformed. In a first step, univariate functions of earthquake activities with equidistant time intervals are defined and are subsequently synchronised with the monitoring series (Hartmann 2005; Hartmann et al. 2005).

Table 2 Factor analysis of measured hydrochemical variables without gases (1977–1998)

	Factor 1	Factor 2	Multiple R ²
<i>Q</i>	(0.64)	-0.40	0.53
PH	0.11	-0.44	0.10
Temperature	0.40	(0.69)	0.46
Cl ⁻	0.97	0.05	0.97
H ₃ BO ₃	0.86	-0.03	0.76
HCO ₃ ⁻	0.96	0.06	0.93
Na ⁺	0.97	0.08	0.96
Ca ²⁺	0.90	0.05	0.90
H ₄ SiO ₄ ⁻	0.15	0.73	0.29
K ⁺	0.39	-0.58	0.40
Mg ²⁺	0.86	-0.17	0.76
Variance	5.85	1.74	
Proportional to the total variance	0.53	0.16	

Last line marks the explained variance of both factors

Table 3 Factor analysis on all measured variables within the time period from 1984 to 1998

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Multiples R^2
Q	0.44	-0.04	-0.01	0.79	-0.11	0.73
PH	0.20	0.02	-0.43	0.13	(0.52)	0.25
Temperature	0.38	0.04	0.74	-0.08	-0.12	0.58
Cl^-	0.96	0.09	0.13	0.15	0.02	0.99
$H_3BO_3^-$	0.92	0.08	0.23	0.17	0.01	0.93
HCO_3^-	0.92	0.07	0.24	0.21	-0.01	0.97
Na^+	0.93	0.09	0.21	0.21	0.02	0.98
Ca^{2+}	0.93	0.09	-0.05	0.16	0.00	0.95
$H_4SiO_4^{2-}$	0.09	0.01	0.81	0.02	0.16	0.37
K^+	0.24	-0.03	-0.12	0.87	0.08	0.65
Mg^{2+}	0.84	0.05	-0.12	0.33	0.04	0.86
Ar	-0.23	-0.80	-0.02	0.10	0.01	0.49
CO_2	0.09	-0.16	0.12	0.44	-0.73	0.96
Gas pressure	(0.48)	-0.69	0.05	0.13	-0.43	0.98
H_2	-0.04	0.05	-0.22	-0.08	(-0.66)	0.07
N_2	-0.25	-0.88	0.06	-0.01	-0.05	0.95
O_2	-0.01	(-0.62)	-0.34	(-0.50)	0.25	0.79
CH_4	0.95	0.11	0.01	-0.07	0.04	0.97
Variance	6.77	2.36	1.77	2.14	1.55	
Proportional to the total variance	0.38	0.13	0.10	0.12	0.09	

Last line marks the explained variance of both factors

Step 1: Transformation of the earthquake time series into a univariate time series

To each individual earthquake a parameter e is assigned. In principle, e consists of (1) an energy component, designating the energy released by the earthquake and (2) a spatial component which expresses the geometrical relation between the rupture point of the earthquake and the monitoring station. For example, $e = M/D_{epicenter}$, where M is the magnitude and $D_{epicenter}$ the epicentral distance. Table 4 shows the herein-used e -transformations. With the exception of the ε -parameter after Dobrovolsky et al. (1979), only simple relations based on basic physical laws were used here. Simple relations allow a more easy interpretation of the results with respect to released energy and geometrical relations. The ε -parameter was chosen because it was successfully used in former studies to quote hydrochemical signals as related to single outstanding earthquakes (Bella et al. 1998). The ε -parameter, after Dobrovolsky et al. (1979), describes the released stress at a site by a single earthquake. It is based on a homogenous half space model assuming a static stress change.

The different weight of energy (magnitude) and geometrical relation has some effect on the interpretation:

If the parameter e is weighted with a component of distance, earthquakes that occur far away possess a lower weight in the analysis. If the energy is represented only by M , strong earthquakes are underestimated, because magnitude is a logarithmic scale. Because this study wants to evaluate specifically, besides the overall seismotectonic activity, the influence of seismotectonic activity related to small events, some parameters are composed of a representation of the energy by the value of M (see Table 4). In addition to analyse possible relations to close earthquake activity some parameters

consists of an energy component represented by M but with a geometrical weight powered by 2 (epicentral distance) or 3 (hypocentral distance).

Step 2: Synchronisation of the two time series

This step involves the synchronisation of the earthquake time series with the spring water time series. For this, a so-called “earthquake activity” $E(e, n)$ is defined, with e , as given above, and n representing a defined interval of time. Relative to a considered sampling time t the earthquake activity E is calculated as follows:

$$E_t(e, n) = \sum_{i=-n}^{+n} e_i, \tag{1}$$

In other words, $E_t(e, n)$ represents the sum of all e -parameters within the considered time interval n (here expressed in days), before and after a sample.

Two cases are exemplarily explained here: $n=0$ means the sum of all e -parameters on day t , and $n=10$ represents the summation of all e -parameters, including all earthquakes within the time interval of day “ $t-10$ ” to “ $t+10$ ” of the representative time t .

In order to reduce the amount of analysis, representative earthquake activity time series E has to be chosen. An appropriate method is to group the E -functions by similarity.

Earthquake activities $E(e, n=0)$ were grouped using factor analysis with varimax rotation (Table 4). If earthquake activities are grouped with high factor loading on a single factor it can be concluded that a high linear correlation exists between them. This allows to use only a few representative earthquake activities within this study for comparison with the hydrochemical time

series. Because Gaussian normal distribution was not given for all earthquake activity functions, results of the factor analysis were checked by analysing, in addition, the correlation matrix.

For further analysis and according to the results of the factor analysis, the parameters $e = \varepsilon = \text{dobro}$ after Dobrovolsky et al. (1979), $e = M/D_{\text{epicenter}}^2$ and $e = M$ were chosen.

Analysis of the relation between earthquake activity and hydrochemistry

Pattern analysis between hydrochemistry and increased earthquake activity E

The first step in the attempt to identify variation in a hydrochemical time series related to earthquake activity is to identify if significant hydrochemical variation and significant earthquake activity E occurs at the “same” time. The earthquake parameter after Dobrovolsky et al. (1979) was efficient to identify major earthquakes coinciding with significant variation in the hydrochemical time series of the spring (Bella et al. 1998). The typical pattern was a “postseismic” increase after close, large earthquakes.

Before significant increase in chloride concentration due to significant increased earthquake activity can be analysed, a suitable criteria must be defined, which allows to estimate time locations of such significant variations. As no standardised technique, until now, exists to evaluate or identify earthquake-related signals, the chloride time series was analysed looking for short-term extraordinary increases, to identify typical coinciding variation patterns in the time series. Eight “peak-like” increases in the chloride time series, marked in Fig. 2 with *a* to *h*, were chosen to estimate typical short-time variation. The average duration of those signals is 20 days with a minimum increase of 20 mg/l. In former studies those signals were claimed not to be related to major close earthquakes (Bella et al. 1998; Biagi et al. 2003).

However, a deeper analysis of the chloride time series reveals the existence of ‘sinus’-like increases (a longer lasting increase followed by a decrease) in addition to those peak-like short-term variations. The shape is similar to those of the ‘sinus’-like increases accompanying five major earthquakes with high amplitude, identified in Bella et al. (1998) in Fig. 3. Because of this finding it was chosen to identify possible signals using a difference-amplitude criteria with a time lag of 10 and 20 days, if chloride concentration was increasing more than 10 mg/l. This is half of the minimum increase of the formerly identified “peak-like” signals. Identified signals were counted as one, if they appear within 20 days. With this definition 27 signals showing unusually high variation in the chloride concentration were identified. They are identified by numbers in Fig. 3 and used for further investigation.

A pre-analysis step compares these signals with the calculated earthquake activity E ($e = \varepsilon$, $n=20$). This pre-analysis shows that most signals coincide with

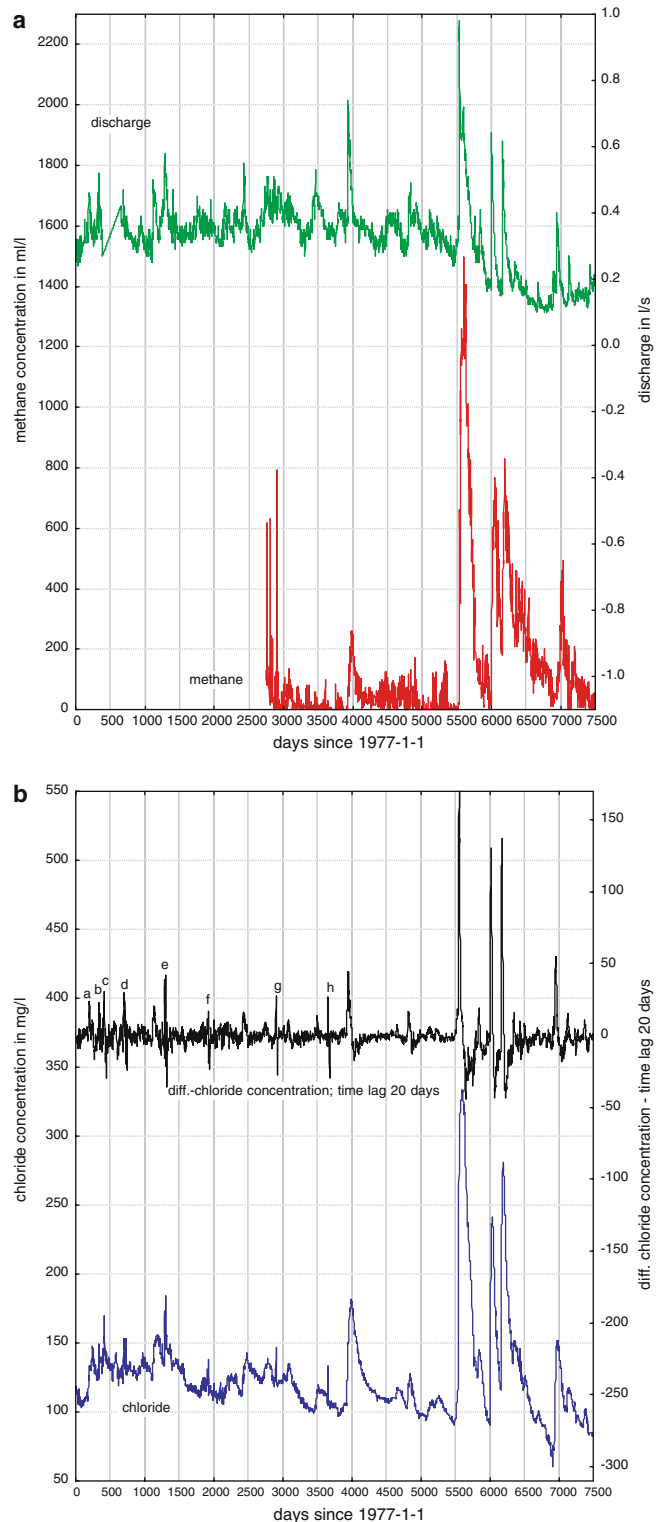


Fig. 2 Comparison of discharge (a), methane (a) and chloride concentration (b). In addition the differences in chloride concentration with a lag of 20 days is displayed (b). Letters *a* to *h* mark peak-like changes in chloride concentration which are discussed in the text

Table 4 e -definitions and results of the factor analysis conducted on E ($e, n=0$)

	Factor 1	Factor 2	Factor 3
M	0.14	0.03	0.96
$\varepsilon_{\text{dobro}}(e = 10^{(1.3 M - 0.173 - 8.19)}/D_{\text{hypocenter}}^3)$	0.94	0.09	0.19
10^M	0.44	0.05	0.72
$M/D_{\text{hypocenter}}$	0.46	0.08	0.85
$M/D_{\text{epicenter}}$	0.75	0.10	0.46
$10^M/D_{\text{hypocenter}}$	0.78	0.10	0.58
$10^M/D_{\text{epicenter}}$	0.94	0.10	0.27
$M/D_{\text{epicenter}}$	0.37	0.43	0.77
$M/D_{\text{epicenter}}^2$	-0.07	0.95	0.05
$10^M/D_{\text{epicenter}}$	0.75	0.24	0.50
$10^M/D_{\text{epicenter}}^2$	0.46	0.79	0.16
Explained variance	4.27	1.82	3.71
Proportional to total variance	0.39	0.17	0.34

M represents the magnitude and D the epicentral or hypocentral distance between the monitoring site and earthquakes

increased earthquake activity summed over 40 days (Fig. 3). Smaller peaks in E are marked with arrows for better identification. Because this pre-analysis seems to support the hypothesis that a long-term connection between hydrochemical variation and earthquake activity exists, the identified signals are analysed further using the earthquake activity functions where parameter $n=0$ (Figs. 4, 5, 6, 7, 8). The focus of this analysis step is to identify if and where chloride signals and increased earthquake activity can be observed within a certain time span.

Because there exists no standard for identifying “significant increased earthquake activity”, the upper 1% quantile in earthquake activity is chosen as a criteria, with values for $e = \varepsilon > 1.5 \times 10^{-8}$, $e = M/D_{\text{epicenter}}^2 > 1.2 \times 10^{-3}$ and $e = M > 20.3$. Later, in a more advanced analysis, sensitivity analysis can help to

optimise the criteria for a relation analysis between both time series.

Different patterns of relations between signals in chloride time series and significant increased earthquake activity E will be classified.

Frequency analysis

In addition to the signal analysis a frequency analysis of both types of time series is provided, using single Fourier transformation with Hamming-window, with the objective of identifying whether there exists shared peaks in their frequencies. This analysis step is used to support the outcome of the signal analysis.

Results

Fifteen of 27 signals in chloride concentration coincide clearly with a locally increased earthquake activity in at least one of the three used earthquake activity functions with the parameter $n=0$ (Figs. 4, 5, 6, 7, 8) within 10 days. This is herein the first criterion for identifying common patterns in both time series.

These signals are marked with ‘1’ in Figs. 5, 6, 7 and 8. However, 6 more signals are accompanied by a clearly increased earthquake activity E with values lower than the 1% quantile, but coinciding with local maxima in E , considering the local distribution of E (marked with ‘2’). With this 21 of 27 signals coincide with increased earthquake activity within 10 days of signal appearance. This can be interpreted as a response of the chloride concentrations to the increased earthquake activities in the signal periods considered. The ε -parameter after the approach of Dobrovolsky et al. (1979) seems to be the most appropriate one of the

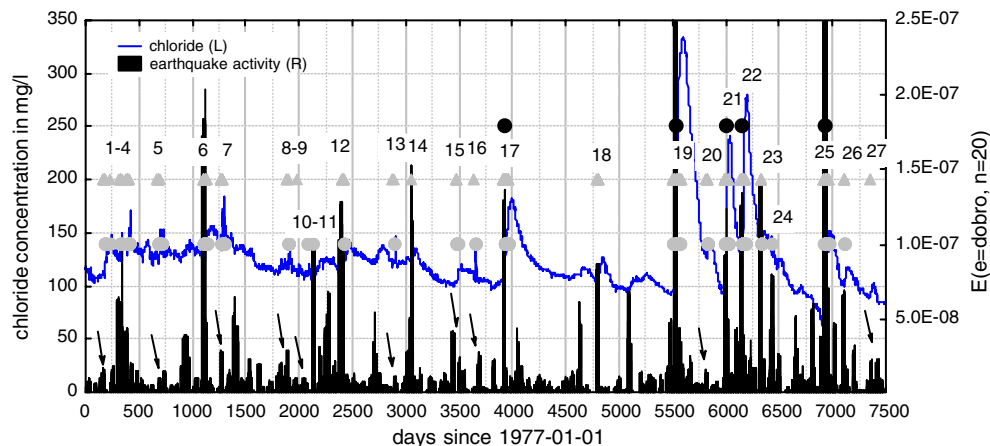
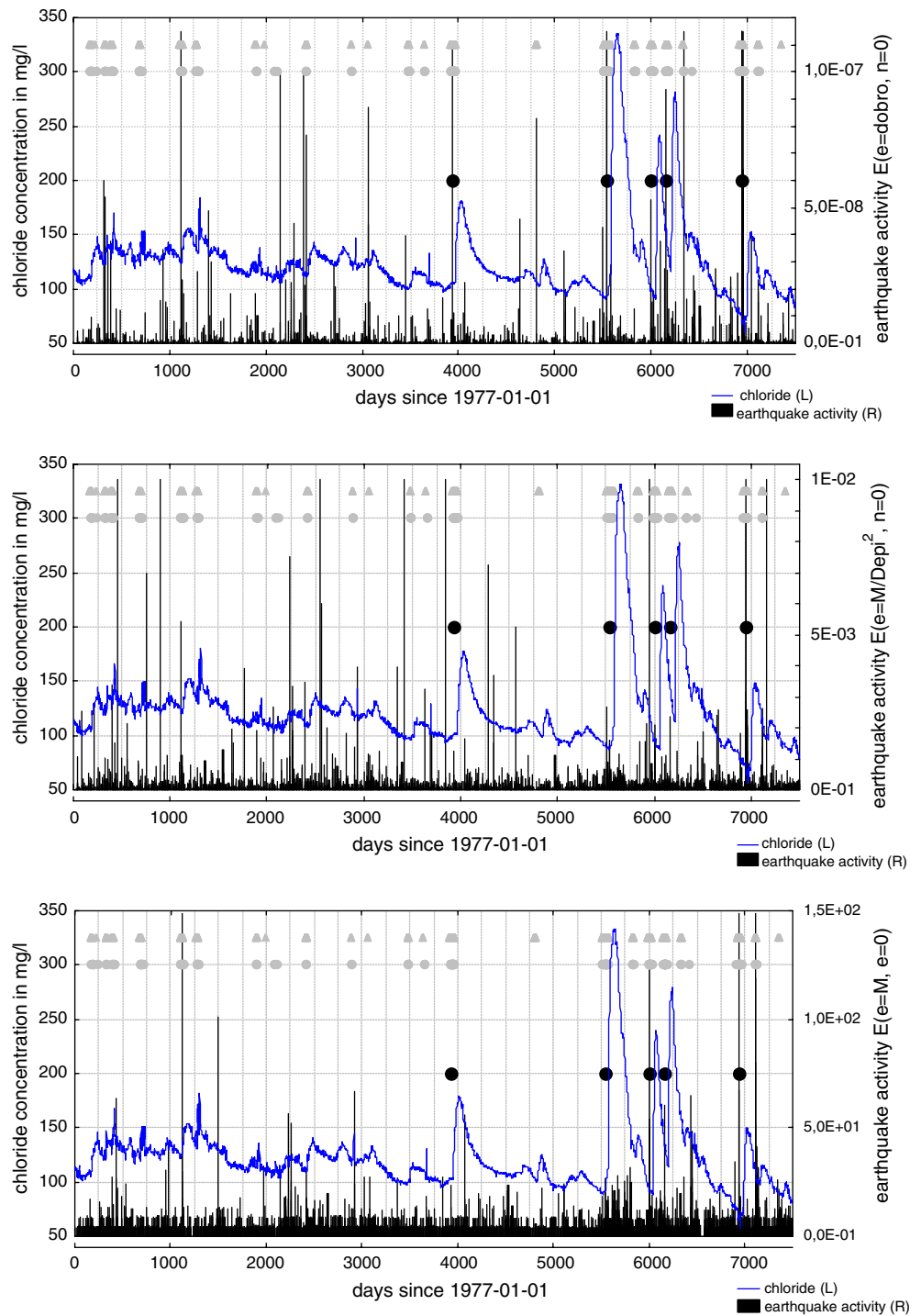


Fig. 3 Chloride concentration in mg/l and earthquake activity E ($e = \varepsilon, n=20$). Numbers 1–27 mark identified chloride signals used for pattern analysis between earthquake activity and chloride time series. Arrows mark increased earthquake activities coinciding with signals in the chloride concentration. Black dots

mark the occurrence of five major earthquakes with $M > 6$ and within a distance of 250 km. Grey dots and triangles mark signals in chloride concentration using as signal criteria a minimum change in concentration of 10 mg/l within 10 and 20 days, respectively

Fig. 4 Comparison of chloride concentration, identified signals in chloride concentration and three selected earthquake activities. *Black dots* mark the occurrence of five major earthquakes within a distance of 250 km with $M > 6$. *Grey dots* and *triangles* mark signals in chloride concentration using as signal criteria a minimum change in concentration of 10 mg/l within 10 and 20 days, respectively

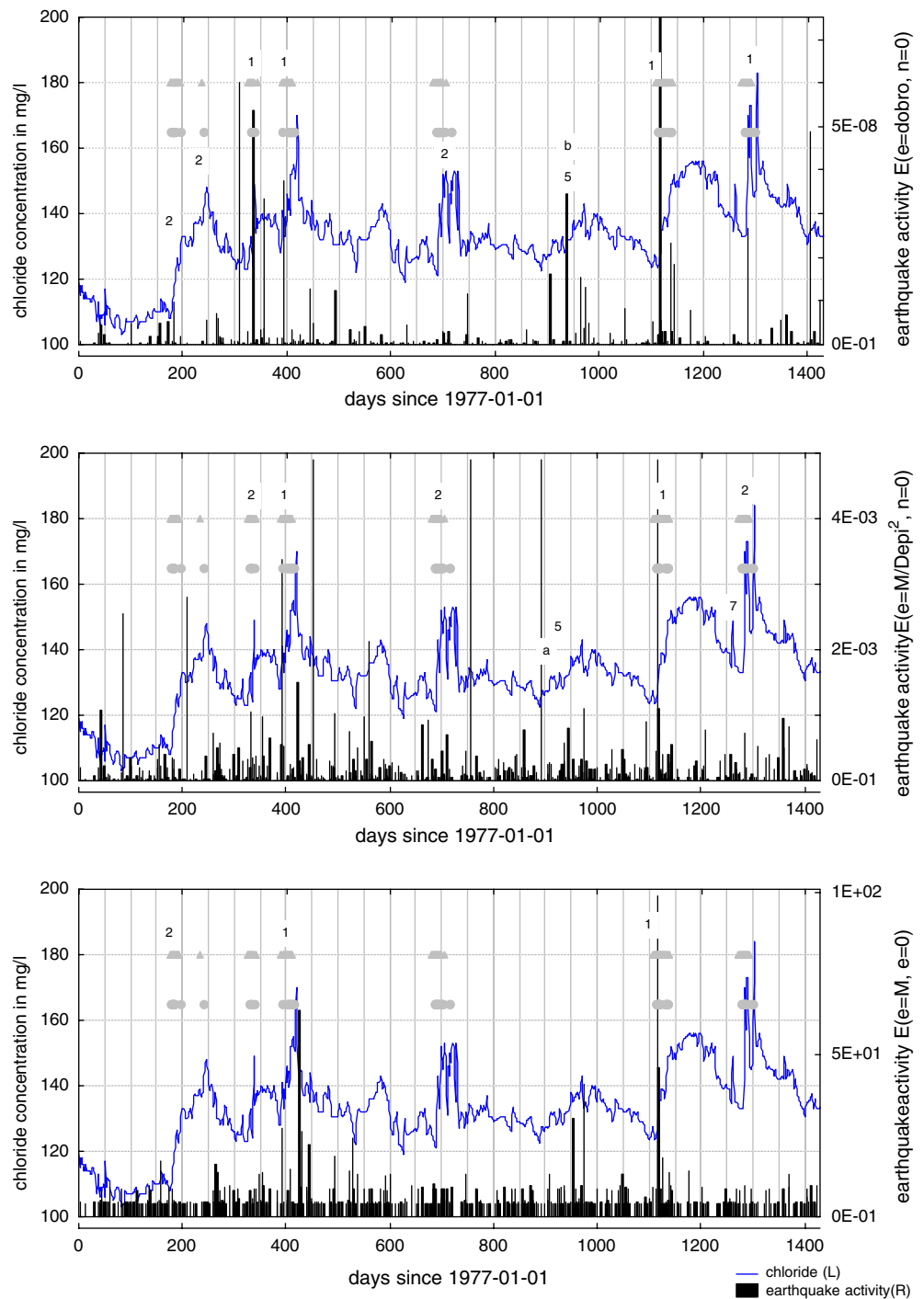


three chosen e -transformations to identify a coincidence between increased earthquake activity and a defined chloride signal. Most of the significant increases in $E (e = \varepsilon, n=0)$, using the 1% criteria, are accompanied by a chloride signal within 10 days. A count on the significant increased earthquake activity values revealed that 35 (of 75, according to the 7,500 analysed days) “significant increased” earthquake activities using

$E (e = \varepsilon, n=0)$ do not appear within 10 days of a defined chloride signal. Using the parameter $e = M/D_{\text{hypocenter}}^2$ and $e = M$ the numbers are 47 and 45, respectively.

However, if signals are analysed in detail, more information can be gained. Two typical patterns of chloride concentration courses related to an increased earthquake activity E can be identified:

Fig. 5 Comparison of chloride concentration, signals 1–7 in chloride concentration and three selected earthquake activity functions between the days 0 and 1,430 since the 1st of January 1977. *Black dots* mark the occurrence of five major earthquakes with $M > 6$ and a distance less than 250 km. *Grey dots* and *triangles* mark signals in chloride concentration using as signal criteria a minimum change in concentration of 10 mg/l within 10 and 20 days, respectively

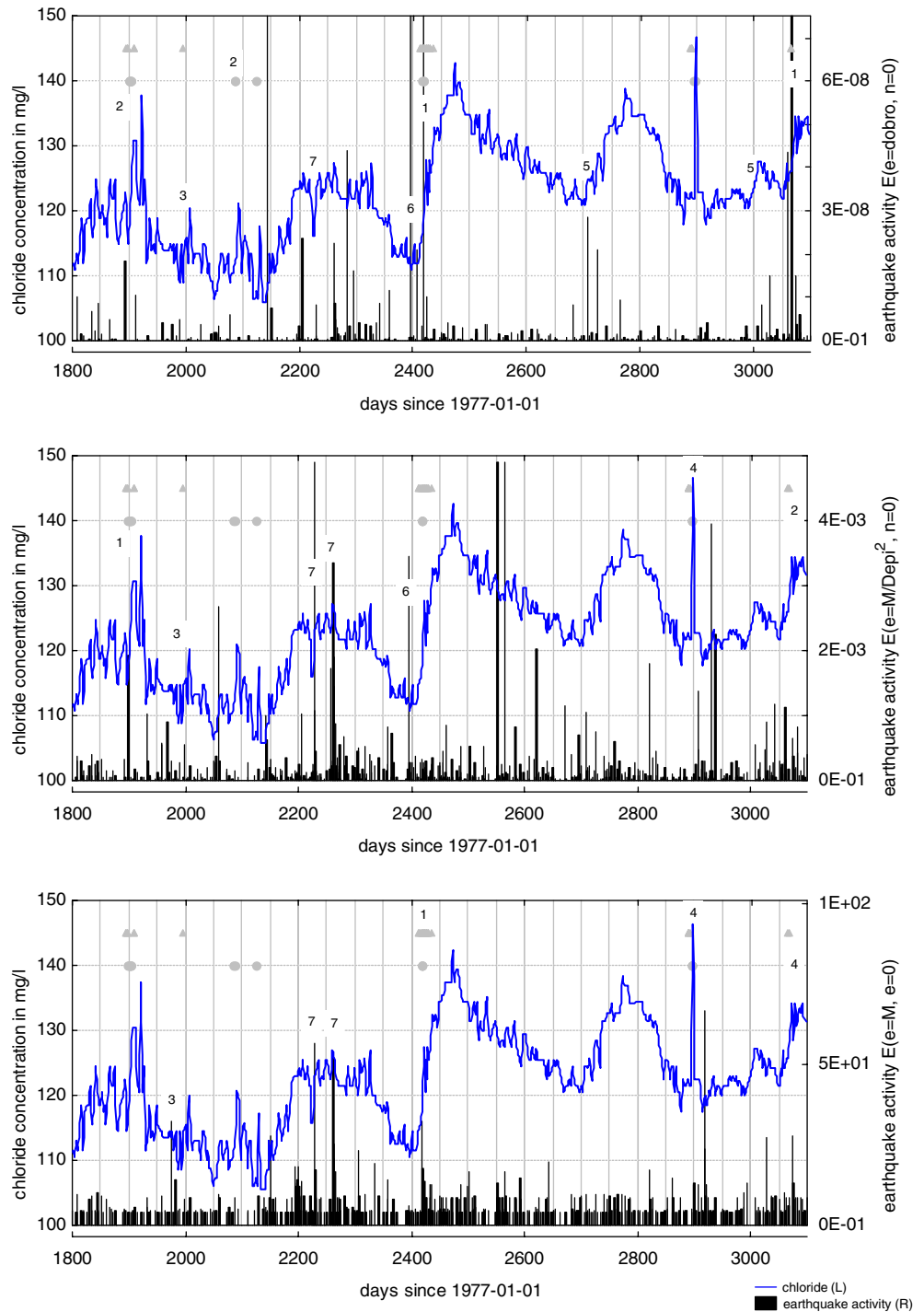


- (a) A peak-like, sharp increase accompanied by a falling back of concentrations; the duration lasts less than 50 days, and
- (b) A sinus-like increase and falling back in concentrations with a duration lasting more than 50 days. In addition, the patterns in chloride concentrations not covered by the signal criteria for identifying coincident patterns in both time series can be observed.

Thus, seven categories of patterns are distinguished herein:

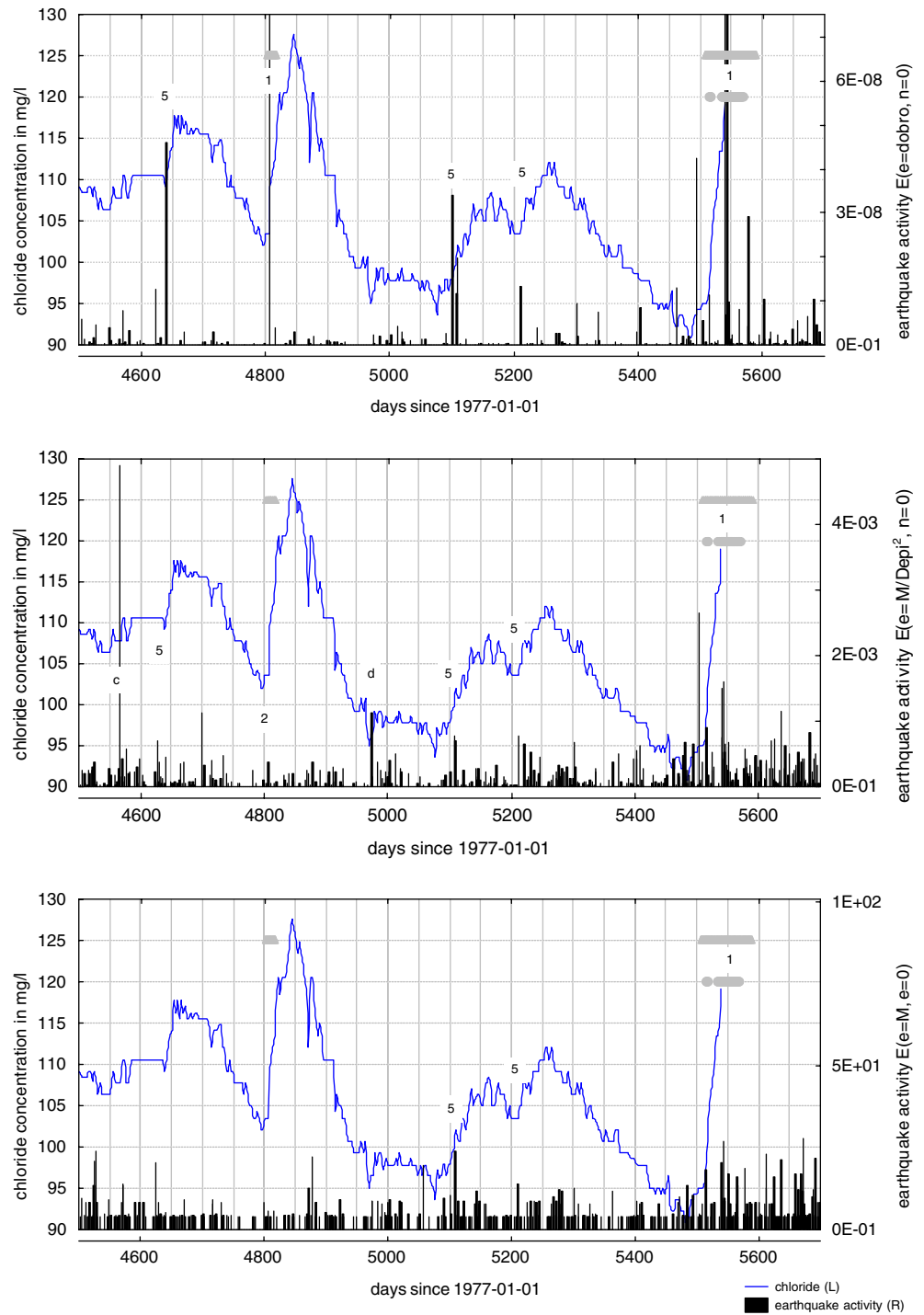
1. A signal in chloride concentration is accompanied by a major increase in at least one of the analysed earthquake activity functions E , belonging to the upper 1% quantile in the distribution of E within 10 days before or after the signal.

Fig. 6 Comparison of chloride concentration, signals 8–14 in chloride concentration and three selected earthquake activity functions between the days 1,800 and 3,100 since the 1 January 1977. Black dots mark the occurrence of five major earthquakes with $M > 6$ and a distance less than 250 km. Grey dots and triangles mark signals in chloride concentration using as signal criteria a minimum change in concentration of 10 mg/l within 10 and 20 days, respectively. The letters “c” and “d” mark change points where the course of the chloride concentration is changing, coinciding with a clear local increase in earthquake activity



2. A signal is accompanied by an increased E not belonging to the upper 1% quantile. But E shows a clear local peak, considering the local E -distribution within 100 days.
3. A chloride signal marks a local minimum in chloride concentration, followed by an increase in chloride concentration, but no clear increase in E (considering the upper 1% quantile) can be observed within 10 days (Fig. 6 only). The signal is neither clearly peak-like nor sinus-like.
4. A signal is accompanied by a major increase in E , not at the beginning of the signal course, but after the signal onset (Fig. 6 only).
5. No signal can be observed, but the beginning of a sinus-shaped course is accompanied by a clear increase in E .
6. No chloride signal can be observed, but an increase in E exists without a chloride signal within 10 days. None of the previous two signal patterns in chloride concentration can be observed.

Fig. 7 Comparison of chloride concentration, signals 18 and 19 in chloride concentration and three selected earthquake activity functions between the days 4,500 and 5,700 since the 1 January 1977. *Black dots* mark the occurrence of five major earthquakes with $M > 6$ and a distance less than 250 km. *Grey dots* and *triangles* mark signals in chloride concentration using as signal criteria a minimum change in concentration of 10 mg/l within 10 and 20 days, respectively



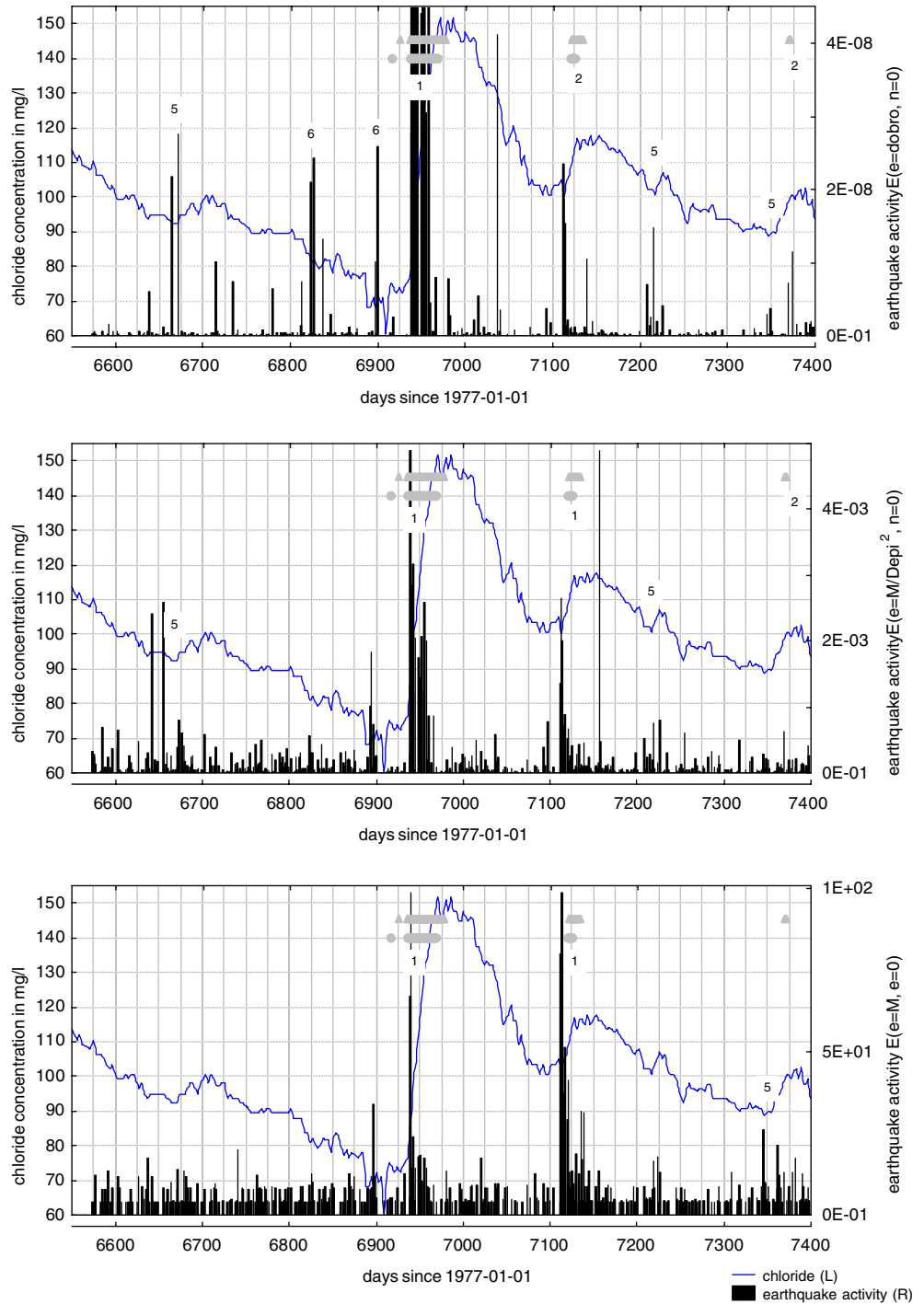
7. No signal can be observed, but a sharp increase in chloride concentration is close to the definition of the signal and is accompanied by an increased E (Fig. 6 only). Examples are marked by classification numbers 1–7 in Figs. 5, 6, 7, 8 and the classification according to each identified signal in the chloride time series is given in Table 5.

As the classification of signals and observed patterns shows the application of aggregated e -parameters over 1

day, $E(e, n=0)$ is an appropriate tool for pattern analysis between both time series.

If the earthquake activity is randomly distributed (white noise) the frequency analysis should show a smooth exponential falling curve. However, if an earthquake activity function E and chloride concentration share spikes at the same frequency it can be assumed that there is a joint pattern underlying both time series. Figure 9 gives an example for this kind of application.

Fig. 8 Comparison of chloride concentration, signals 25–27 in chloride concentration and three selected earthquake activity functions between the days 6,500 and 7,400 since the 1 January 1977. *Black dots* mark the occurrence of five major earthquakes with $M > 6$ and a distance less than 250 km. *Grey dots and triangles* mark signals in chloride concentration using as signal criteria a minimum change in concentration of 10 mg/l within 10 and 20 days, respectively



Twelve spikes which coincide in both frequency functions are marked with a vertical line. The large number of coinciding spikes support the interpretation that the earthquake activity functions represent seismotectonic processes, with relation to the variation in hydrochemistry of the spring. The marked spikes in the frequency functions represent periods between 50 and 660 days.

The lower period may be related to the sinus-shaped increases due to increased earthquake activity, as they often last around 50 days. The upper period duration

may be the result of the long lasting changes in the second half of the time series due to the coincidentally increased earthquake activities lasting relatively long and marking the start of the increase in chloride concentration, which can exceed 100 mg/l.

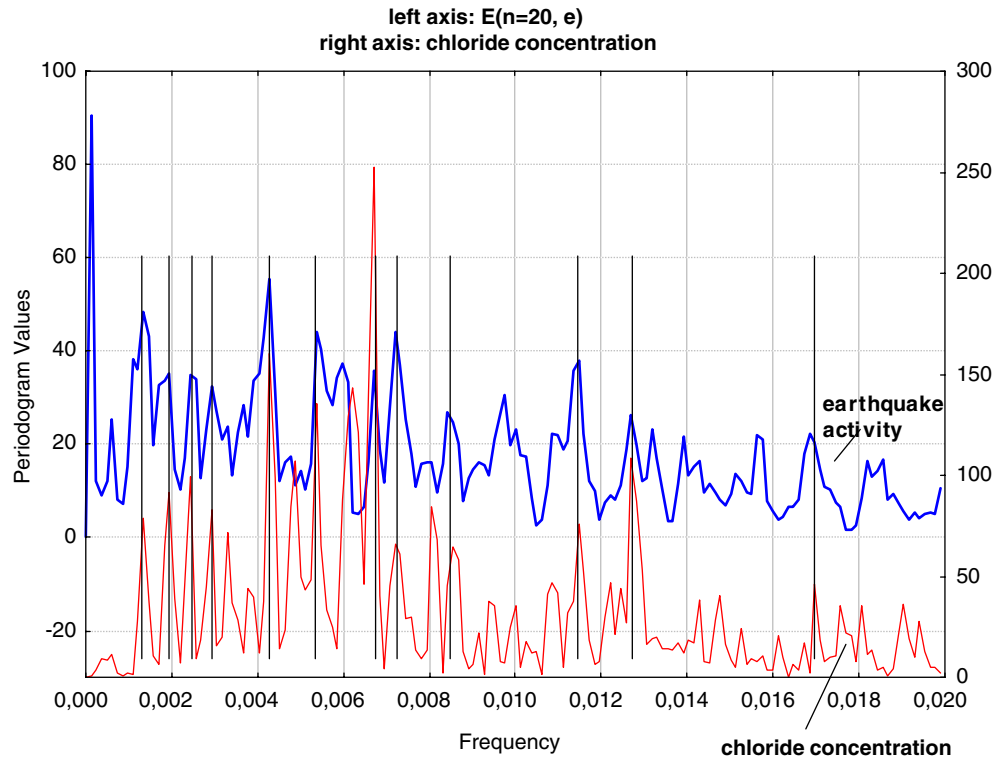
This supports the result from the pre-analysis: long lasting increases in chloride concentrations coincide with periods of increased earthquake activity. However, no short-term patterns, represented by peak-like patterns in chloride concentrations, are identified. This

Table 5 Identified signals in chloride concentration and the according signal pattern type as explained in the text

Signal no.	$e = \varepsilon$	$e = M/D_{epicenter}^2$	$e = M$
1	2	—	2
2	2	—	—
3	1	2	—
4	1	1	1
5	2	2	—
6	1	1	1
7	1	2	—
8	2	1	—
9	3	3	3
10	2	—	—
11	—	—	—
12	1	—	1
13	—	4	4
14	1	2	4
15	—	—	—
16	4	4	4
17	1	1	1
18	1	2	—
19	1	1	1
20	3	3	3
21	1	1	1
22	1	—	—
23	2	—	—
24	1	1	1
25	1	1	1
26	2	1	1
27	2	2	—

can be due to the aggregation of earthquake activity with $n=20$. Frequency analysis conducted using $n=0$ showed no clear shared spikes in the distribution of frequencies.

Fig. 9 Spectral analysis of the chloride concentration and the earthquake activity E ($e = M/D_{epicenter}^2, n=20$). Vertical lines mark frequencies where peaks in both frequency functions coincide. Those spikes represent periods between 50 and 660 days



The comparison of chloride and methane concentrations in Fig. 2 reveals a parallel course in the major amplitudes accompanied by 5 close, major earthquakes (Fig. 3). Thus, it can be concluded that the cause for the change in aquifer chemistry is influencing both, mixing aquifers and gas exhalation of the earth’s crust.

Discussion

Results indicate (a) a long-term influence (>2 decades) of seismotectonics on hydrochemical variation in the sampled spring and (b) observed seismotectonic activity related to the hydrochemical variation is not necessarily leading to an eruption of the close volcano. This outcome declares the applied analysis approach as a suitable tool for the analysis of “earthquake–volcano interactions”, using the hydrochemical time series from sites located close to volcanoes in pre-eruption stage.

Distribution of seismic events, mirroring regional tectonic settings, has an impact on the creation of earthquake-related signals, as differences in the relation patterns reveal when the three used e -parameter definitions are compared.

The herein used e -transformations cover different weights for the parameters, distance and magnitude representing the released energy of single earthquakes. The e -parameter after Dobrovolsky et al. (1979) is representing the strain–stress release in a theoretical earthquake preparation zone based on a homogenous

half-space model. The equation for the calculation of ε underestimates small events and weights a seismic event by the hypocentral distance. The second used e -transformation $e = M/D_{\text{hypocenter}}^2$ is overestimating close seismic events using the epicentral distance. However, most earthquakes are correlated with the subduction zone (Fig. 1). The e -parameter $e = M$ can be interpreted as a relative counter of earthquake activity within the analysed system, covering all events within the 1,000 km distance, as the magnitudes in the used earthquake catalogue are mostly between 4 and 6.

The parameter ε seems to be most suitable for analysing relations between both types of time series as it shows the most relation patterns of category type 1 (Table 5). However, the other two earthquake activity functions also show some clear relations to significant variation in the chloride time series, which is not clearly covered by the ε -parameter (e.g. case “a” and “b”, in Fig. 5 or case “c” and “d” in Fig. 7). A clearly increased earthquake activity in the middle part of Fig. 5 displays an onset of a type 5 pattern, which is not clearly covered by the ε -parameter. However, approximately 50 days later a clear increase in the latter earthquake activity definition (case “b” in the upper part of Fig. 5) can be observed. In coincidence with the increased earthquake activity in case “b”, a small sharp increase in chloride concentration can be observed. This example reveals that the probable mixing of signals in chloride concentration after increased earthquake activities represents a problem in this kind of relation analysis and should be considered.

There are at least two possible causes why not all identified signals are correlated with an increased earthquake activity and vice versa:

- (a) The chosen e -transformations are not sufficient and/or
- (b) Other processes than earthquake activity were neglected, but have a significant influence on the hydrochemical variation. Other factors capable of influencing variation in hydrochemistry are, e.g. hydrology or earth tides. A future, improved, model should consider all processes which may affect the hydrochemical composition of the spring.

The pattern analysis comparing the course of the chloride concentration and different earthquake activities E suggests that different types of responses in chloride concentration to changed aquifer conditions should be considered. This observation is essential if analysis should be improved, e.g. if the methodology should be implemented into a volcano monitoring programme.

The herein chosen earthquake transformations are relatively simple as they consider only released energy and the geometric relationship between the monitoring site and the location of each earthquake.

Identification of the improved e -parameters for the introduced approach represents a classical problem in

signal analysis. It should be considered that even with incorporating physical models not one e -definition is sufficient for matching with the variation in the hydrochemical time series. This is because triggers to changes in aquifer conditions are possible due to different processes as discussed in introduction: first, by static stress changes caused by earthquake activity, second, also by possible triggered processes in the magma chamber of the volcano and third by dynamic triggered stress changes in the earth’s crust induced by the earthquake activity (e.g. Hill et al. 2002). In addition, it should be considered that the analysed system is changing over time.

From the results it becomes clear that the formerly used static stress model, considering only single earthquakes, is not sufficient to explain the signals in chloride time series accompanied by increased earthquake activity in the first half of the time series. During this time period no major earthquake with $M > 6$ within a distance of 250 km was observed. Those earthquakes were claimed to be capable of triggering strain stress changes, based on a homogenous half space model, large enough for resulting in signals in the chloride time series (Bella et al. 1998).

In addition, models of viscoelastic relaxation and dynamic triggering (e.g. Hill et al. 2002) should be considered if physical models should be adopted in future, more advanced analysis.

Moreover, the analysis could be improved by testing different selections of earthquakes from the earthquake catalogue. This may be the consideration of knowledge from volcano-related earthquake activity or regional and local tectonic settings.

Another possibility to improve the relation analysis is to use different techniques for grouping E -functions: e.g. by grouping only a subset of the E -values of each E -function (e.g. the highest values) or by transforming E -functions to Gaussian normal distribution before grouping with parametric statistical techniques.

Even if other possible influences on the hydrochemistry of the spring water were neglected (e.g. earth tides, rain fall, etc.) results are significant.

The type 4 pattern is by definition a precursory pattern to follow increases in the calculated earthquake activity functions E . Only two such cases were identified herein (signals 13 and 16 in Table 5; Fig. 6). The search for such type 4 patterns might be a suitable application for the search of earthquake precursory signals. The herein analysed time series did not show enough type four patterns to conclude that earthquake precursory signals appear frequently. As the example of case “a” and “b” (Fig. 5) shows a mixing of reactions/signals in chloride concentration due to increased earthquake activity is probable.

In addition there might exist problems in the interpretation of signal–earthquake activity relations if possible errors in the time series are taken into

account. The signals 13 and 16 represent spike-like signals based on only one value. There is not enough information to account these phenomena to other, unknown influences. However, both signals appear within a period of increased earthquake activity as Fig. 3 shows.

Conclusions

It can be shown that processes leading to seismicity have a long-term effect on the variations in the monitoring time series during the observation period. The frequency analysis underlines these findings. From this it can be concluded that seismotectonics represents a factor, which is directly or indirectly inducing variation (e.g. earthquake–volcano interaction) in the composition of the spring water composition, besides other possible factors like aseismic processes, earth tides, temperature or rainfall. The covariation patterns of chloride and methane suggest that seismicity might not only have an effect on the magma chamber below the volcano but can also be attributed to changes in the permeability of the earth's crust.

Different definitions of earthquake activities using variant definitions of e -parameters were used for calculating earthquake activity functions $E(e, n)$. The pattern analysis revealed that the chosen transformations of earthquake information are sufficient to identify coincidence between increased earthquake activity and signals in the chloride time series. No earthquake activity function alone coincides with all discussed signals in the chloride concentration, as shown in Figs. 4, 5, 6, 7, 8. This reflects the temporal–spatial complexity of the relationship between processes leading to seismotectonic activity and the variation in monitoring time series.

Despite this, the results show a clear influence of processes, related to increased seismotectonic activity, on the hydrochemical composition lasting longer than 20 years. The applied methodology can be used to analyse historical hydrochemical data sets and to test a monitoring site, if it is sensitive to seismotectonic-related processes. Thereby every monitoring site may or may not show relations to chosen definitions of earthquake activities, depending on regional seismotectonics and local geological settings.

Results indicate that the proposed methodology is useful in supporting the analysis of earthquake–volcano interactions, not necessarily focusing on (a) major earthquakes triggering eruptions or (b) classical physical models based on shear dislocation and linear elasticity of the earth's crust.

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