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Organohalogen emission from saline environments – spatial extrapolation using remote sensing as most promising tool

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Abstract

Due to their negative water budget most recent semi-/arid regions are characterized by vast evaporates (salt lakes and salty soils). We recently identified those hyper-saline environments as additional sources for a multitude of volatile halogenated organohalogens (VOX). These compounds affect the ozone layer of the stratosphere and play a key role in the production of aerosols. A remote sensing based analysis was performed in the southern Aral Sea basin, providing information of main soil types as well as their extent and spatial and temporal evolution. VOX production has determined in dry and moist soil samples for 24 h. Several C1- and C2 organohalogens, including chloromethane and bromomethane, have been found in hyper-saline topsoil profiles. The range of naturally produced organohalogens includes dichloroethene. For the 15 000 km^2 ranging research area in the southern Aralkum desert a daily production of up to 23 t dichloroethene has been calculated using MODIS time series and supervised image classification. The applied setup reproduces a short-term change in climatic conditions starting from dried-out saline soil, instantly humidified during rain events or flooding. VOX emission from dry fallen Aral Sea sediments will further increase since the area of salt affected soils is expected to increase in future. Opportunities, limits and requirements of satellite based rapid change detection and salt classification are discussed.

1 Introduction

Organic compounds containing halogens – especially chlorine – have been considered for a long time to be of industrial origin only, and it was assumed that humans could easily control the production and emission of these compounds in case they would cause a threat for life on Earth. Recent environmental problems such as stratospheric ozone destruction and the increasing pollution of the biosphere through volatile organohalogens (VOX) are considered to have a large impact on the well-being of mankind. VOX are effectively linked to atmospheric chemistry cycles, leading to potentially significant

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feedbacks on cloud formation, Earth's albedo and eventually the regional and global climate.

Since the middle of the 70's it became clear that some reactive organohalogens are purposefully produced by nature e.g. in soils and sediments of hyper-saline salt lakes (Winterton, 2000; Gribble, 2010; Schöler and Keppler, 2003; Weissflog et al., 2005). To date, the natural production of more than 4714 different organohalogens is known, involving biogeochemical, biochemical and microbial processes (Gribble, 2010). This includes de-novo producers like fungi, halophilic bacteria and archaea, plants, animals, and insects.

In addition to volatile alkyl halides and polar organohalogens such as haloacetates, there is evidence that even semi-volatile organohalogens can be naturally formed from humic substances through abiotic geochemical processes. For instance nature's production of chloromethane (5–6 Mt) exceeds the anthropogenic production (50 Kt) by a factor of 100 (WMO, 2007).

While anthropogenic organohalogen pollution is certainly an important issue and the ban of some compounds as stipulated in international treaties have to be carefully controlled, it is high time to commence with a comprehensive study of the natural release of organohalogen species, in particular to the lower atmosphere and the terrestrial environment. The importance of very short-lived halogenated substances (VSLS) for the budget of stratospheric bromine was emphasized by WMO (2007). Many of these VSLS are of natural origin.

Relevant data on the quantity and variety of low molecular weight organohalogens in the terrestrial environment are limited. This compartment receives significant fluxes of inorganic halides via the deposition of sea salt aerosols and from combustion processes, and in addition from weathering processes of rocks. Due to the lower concentrations of halides in soil (except for peaty and saline soils) natural halogenation processes in the terrestrial environment have been assumed to be a VOX source of minor importance. However, there is evidence that natural halogenation is a widespread phenomenon in some terrestrial environments.

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There have been a number of studies that have dealt with the release of organohalogens from coastal marshes and other wetlands, where halogenation was suggested to depend on fungal and bacterial activity (e.g. von Glasow and Crutzen, 2007). Besides biotic formation of organohalogens there is also increasing evidence of an abiotic formation in soils involving humic substances and iron (Keppler et al., 2000, 2004; Huber et al., 2009). Although the exact mechanisms leading to the abiotic formation of organohalogens, e.g. the potential role of radicals and reactive humic and Fe species are still not fully understood.

There is a number of studies that tried to come up with budgets for longer-lived halocarbons, mainly of interest for stratospheric chemistry, including emissions from peatlands (e.g. Dimmer et al., 2001), wetlands (Varner et al., 1999), salt marshes (Rhew et al., 2000), and terrestrial vegetation (Yokouchi et al., 2000, 2002; Hamilton et al., 2003). It is not clear if further polyhalogenated C1-organohalogens such as CH_2Cl_2, $CHCl_3$, and CCl_4 or even C2-organohalogens such as tri- and tetrachloroethene are formed during the decomposition of dead organic matter in soil.

Research has so far mainly focussed on regions polluted by humans and on coastal areas. Thus the global source strengths of organohalogens from soils and vegetation are poorly constrained. Keppler et al. (2005) highlighted the need for a better quantification of long-lived halomethanes such as CH_3Cl and CH_3Br from recently discovered, additional natural terrestrial sources. For example, Wishkerman et al. (2008) elucidated the reaction of plant pectin with bromide forming CH_3Br. This appears abiotically at ambient temperatures with the observed emission to doubled with every 5 °C rise. Elevated concentrations of CH_3Br and $CHCl_3$ have been proven for hyper-saline sediments of southern Russian and Kalmykian salt lakes (Weissflog et al., 2005). These results have important implications for the VOX release from vegetation and soils located in regions that are particularly affected by climate change (i.e. heat waves and drought). However, the global source strength still remains uncertain. The main driver behind the mentioned biogeochemical VOX production can be attributed to pH-level, salt content, salt composition (halide, sulfate, carbonate) as well as soil humidity, respectively soil

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water content, and organic content.

Some VOX or their metabolic degradation products exhibit a phytotoxic potential, where infected plants show increased plant transpiration, early senescence, decreased plant growth and overall lower plant vitality. Especially in combination with drought stress episodes and soil salting this can accelerate desertification.

Thus, the emission and deposition of VOX to and from the atmosphere can strongly influence the functioning of terrestrial ecosystems (e.g. Lange et al., 2004).

Beside the intensified public discussion on the trustability of climate models and their outcomes, there is no doubt that the predicted climate change will send his first indications within the next few decades. Towards the end of the 21st century a clear increase of dry areas is expected for Middle Asia as well as for Africa, as shown in Fig. 1. For both regions the current situation of land degradation and desertification becomes more problematic due to a constant anthropogenic influence, such as overgrazing, pollution and physical overstraining. In some regions the proposed climate change will lead in consequence of higher temperature, more frequent heat waves, lower rainfall and higher evaporation to an increase in quantity and scale of hyper-saline salt lakes, salty soils and salt-dust storms. Due to their negative water budget most recent semi-/arid regions are characterized by vast evaporates (salt lakes) and salty soils. Thus number and size of saline ecosystems will increase from the time when deserts and semi-deserts start spreading, as it observable e.g. in Middle Asia.

In consequence the question emerges whether and how recent and future saline terrestrial ecosystems will have an impact on global VOX budget, including seasonal effects like dissolving of halite minerals during rain events followed by recrystallization, as well as annually shifting soil temperature and soil humidity.

For the first time this study aims to combine remote sensing and VOX emission data to examine the potential of satellite products for estimation of regional VOX emission loads from hyper-saline environments.

To extrapolate small-scale experiments to supra-regional and global scales it is necessary to provide spatial information on number, size, and seasonal dynamic of saline

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ecosystems. Obviously satellite based remote sensing seems to be the method of choice, since the knowledge on spatial distribution and dynamic of surface salt types allows to extrapolate small scale VOX emission data to regional and global scales.

Within this study hyper-saline ecosystems of different geographical origin, different geochemical character and different development states have been compared for VOX production potential. The Central Asian Aralkum, whose soils have been tested for VOX production, serves as a perfect example for a highly dynamic, spreading saline ecosystem, composed of hyper saline crusts and saline soils which appeared after desiccation of the Aral Sea (Fig. 2). Additionally remote sensing based analysis was performed in the southern Aral Sea basin, providing information of main soil types as well as their extent and spatial and temporal evolution.

2 Methods

2.1 Study Area

The study area (Figs. 2 and 3) is located within the autonomous Republic of Karakalpakstan (Uzbekistan), covering an area of approximately 15 000 km^2. With the regression of the fourth largest sea of the world, a huge new saline desert emerged on the former seabed, which is called the "Aralkum" (Breckle et al., 2001). Former harbour cities like Muynak (Uzbekistan) are now located tens of kilometers away from the present shoreline. From a ecological point of view, it is considered as the world's largest area where primary succession is taking place (Wucherer and Breckle, 2001). Decreasing water flow in the Amu Darya river (the Oxus of ancient times) caused dramatic loss of wetlands and the associated reed communities in the rich ecosystem of the Amu Darya river delta (Sivanpillai and Latchininsky, 2007). The shrinking Aral Sea exposed about 50 000 km^2 of its former seabed (Micklin, 2007), which shows a wide variety of different landscape and soil types. The major part of the desiccated seabed is considered as highly unstable landscape with a high ecological hazard in terms of

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desertification and eolian erosion (Dukhovny et al., 2008). Salt affected areas in particular appear after recession (e.g. a wide variety of Solonchaks and Takyrs), which are considered as a major source for salt – and dust storms in the region (Razakov and Kosnazarov, 1996; Orlovsky et al., 2001; Singer et al., 2003; Mees and Singer, 2006).

2.2 Monitoring land cover dynamics

Classification of Terra MODIS time-series was performed to assess the land cover dynamics in the study area between 2000 and 2008 and to monitor different stages of soil salinization. The MOD09 8-day Surface Reflectance Data of the Terra MODIS satellite (Moderate Resolution Imaging Spectroradiometer) was chosen as primary data source. Seven spectral bands, centered at 648 nm, 858 nm, 470 nm, 555 nm, 1240 nm, 1640 nm, and 2130 nm respectively, were processed to obtain the full spectral range and improve class separability. The almost daily availability of MODIS satellite images since the year 2000 enables recording landscape dynamics in a very high temporal resolution. Ground reference data for classification of satellite images were collected during field surveys in the study area in 2007, 2008 and 2009 in accordance to the FAO LCCS (Land Cover Classification System), whereas 650 ground reference points were collected, including photos of the sampling sides, vegetation mapping and important soil characteristics. A quality assessment of the input data was performed, using the TiSeG software (Time Series Generator) (Colditz et al., 2008). Additional input information for the classification procedure was provided through the calculation of the NDVI (Normalized Differentiated Vegetation Index) and several band ratios where tested and evaluated for their potential to improve discriminating salt affected areas. Besides data noise, time series exhibit significant temporal autocorrelation. In order to reduce the redundancy in feature space, metrics (basic statistics such as mean, standard deviation, minimum, maximum, and range) were calculated and further used as baseline dataset for the classification. Decision trees (DT) were found to be the most suitable method for classifying the input data, and have successfully been applied in other studies (DeFries et al., 1995; Hansen et al., 2000). The classification of the time series was conducted

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with the QUEST algorithm (Quick Unbiased Efficient Statistical Tree) (Loh and Shih, 1997), which is implemented in the software add-on "RuleGEN 1.02" running in the standard image processing environment "ENVI" (ITT Visual Information Solutions).

The classification results were used to perform a post-classification change-detection analysis for the time steps 2000–2004, 2004–2008 and 2000–2008. The approach used in this study provides "from-to" change information and the kind of landscape transformation that have occurred. The land-cover change areas between the different classes were then calculated. Validation was performed using an independent sample of validation points to assess classification accuracy. Validation points from 2008 were measured directly in the field, whereas for 2000 and 2004, validation points were randomly generated and evaluated visually using Landsat TM imagery and NDVI temporal signatures. For further details of the method see Löw et al. (2011).

2.3 Soil chemistry and VOX emission

Soil samples for VOX analysis have been taken in May 2009. After pre-screening certain soil types in the study area using Landsat 5 TM classification based soil maps (Dukhovny et al., 2008), specific sample sites have been selected during travelling several transects, focusing on unaffected natural topsoil. Three topsoil profiles were sampled for each site: 0–2 cm, 2–4 cm and 4–6 cm. Where available the soil/salt crusts were additionally sampled between 0–0.5 cm. The sampling scheme may not fulfil geological requirements, but allows comparing sample sites around the globe. Sampling sites were positioned by means of GPS measurements including photos of the sampling sites, soil surface characterization and geo-botanic mapping by a standardized form sheet based on LCCS.

Soil samples where kept cool and shipped to Heidelberg (Germany), then freeze dried and milled. XRD analyses have been performed applying a Bragg-Brentano powder diffractometer (Philips PW 3020 Goniometer) with secondary beam monochromator. Soil organic carbon content was calculated from total carbon content and inorganic carbon (carbonate), using a CNS analyzer (Vario Max,

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Elementar/Germany), respectively a carbonate bomb (Müller and Gastner, 1971).

Determination of VOX production in topsoil samples followed the procedure described by Huber et al. (2009). In brief, dried and milled soil samples were transferred to 20 ml headspace glass vials and incubated for up to 24 h at 40 °C. After incubation the VOX production has been determined using a custom made purge & trap system, connected to a gas chromatograph with mass spectrometer (Varian STAR 3400 GC and Saturn 2000 ion trap MS). To discover the effect of soil humidity different assays have been performed, adding distilled water to selected soil samples or directly testing the dried soil.

3 Results

Using MODIS time series and supervised image classification, different stages of salinization were classified for the years 2000, 2004 and 2008, ranging from salt crusts within a narrow stripe adjacent to the see, to extensive Solonchaks an almost salt free sand sheets. Overall accuracies were consistently high with 82.8 %, 81.5 % and 79.5 %, and Kappa statistics of 78 %, 77 % and 73 %, respectively. It is shown that the recession of the Aral Sea results in a quick build up of extensive salt crust directly adjacent to the sea. Almost all of these salt crusts converted into a series of different Solonchak types and then, in some parts of the area, further into almost sand free bare areas. This trend was found to occur within 8 years at some locations, demonstrating that a significant proportion of the former seabed features highly unstable surface types (Fig. 3). The changing hydrological situation of wetlands over the years is obvious (Fig. 2). Important types of land cover change between 2000–2004 and 2004–2008 were “water to salt soils”, “water to salt crusts” and the conversion of salt soils to bare area (Tabel 1).

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Mineral content of the 0–2 cm topsoil layer only, including salt crusts, have been determined for selected sites within the study area (compare to Fig. 3). The composition of main minerals, calculated through XRD semi-quantitative analysis is given in Fig. 4. All locations, except T3, are dominated by SiO_2-Minerals (sand: 47–83 %). Location T3 itself is situated within the rapid developping salt crusts surrounding the residual water body of Aral Sea and is dominated by precipitated salts (sulphates 35 %, halides 32 %, carbonates 20 %). Compared to that T6 represents typical sandy topsoils dominated by 83 % silicates with only 10 % sulfates and 7 % carbonates. The area surrounding T6 dried out very recently and is a region that's influenced by accumulation of sand and aeolian dust. Locations T7 and T5 can be seen in an intermediate class with ~50 % silicates, versus ~20 % carbonates and ~15 % halide. Both sites are being flooded regularly (T7, storage lake Sudochie) or constantly influenced by increased soil humidity and elevated level of saline groundwater (T5, next to old, temporally flooded dam). Through capillary power these humid soil accumulates salt at the soil surface, forming distinct crusts of several mm thickness.

Soil organic content, mainly important for VOX production, only reached very limited amounts. The lower limits with 0.2 %, 0.3 % and 0.5 % were found for recently dry-fallen sandy soils T6 and T10, as well as the lately appeared salt crusts of T3. Highest Corg values were found in dry sediments of the water reservoir Sudochie, location T7. Accordingly T7 has to be compared carefully with other "salt soils" in the study area – e.g. T5 and T10, which gave the similar RS-signal but provide different hydrological features.

VOX emission experiments were performed at each 0–2 cm level. As shown in Fig. 4 most soil samples produce dichloroethene (DCE) in the range of 100 ng m^{-2} within 24 h after humidification. DCE serves as proxy for further VOX such as halogenated methanes and ethanes/ethenes. DCE is widely known as breakdown or degradation product of anthropogenic VOX pollution, particularly in groundwater and soils. Data of Fig. 4 and Table 3 reveal the frequent emission of DCE from several saline environments in Middle Asia, Africa and Southern Russia, but the confirmation of a natural

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production process is still pending. DCE might also be produced through degradation of higher chlorinated precursors such as tri- and tetrachloroethene and trichloroethane, since recent research has revealed chemically-precipitated ferrous iron to act as an abiotic active reductant for VOX (e.g. Brown et al., 2009).

Regarding Fig. 4 the newly formed sandy soils of the locations T6 and T10 do not show any DCE formation, which meets the findings of very low C_{org} content. Surprisingly soil T7, which shows highest measured C_{org} contents and provides favourable high soil humidity did not display any DCE production as well. On the other hand T11, a rather sandy soil type, but several ten years matured after desiccation, reached highest DCE values. T11 is situated southeast of Muynak and lies within the former Amu Darya river delta. Desiccation after 1970–1980 and regularly flooding during spring time was followed by usage for live-stock feeding. However, the driver behind DCE production and possible counterproductive factors remains unclear.

Employing dichloroethene as agent for a rough estimation of regional VOX emission potential, the land cover class data of Tabel 1 are combined with the DCE formation data of Fig. 4. Resulting calculated DCE emission data for the years 2000, 2004 and 2008 displays Table 2. Emission data refer to a 24 h production time under the favourable condition of a moist soil system (e.g. after flooding or rain events) and elevated summer temperatures of 25–35 °C air temperature, resulting in a topsoil temperature of up to 50 °C. Due to difficult sampling conditions close to the remaining water body, no samples could be taken for the land cover class "Water". Land cover class "Reed" was not included as well. For class "Shrubland" and "Bare areas" more than one sample was taken. Their corresponding emission loads vary drastically between the different samples sites, but all of them have been classified to the same land cover class. Obviously there are limits in the applied land cover classifying method, since it is difficult to distinguish between differences in salt composition and soil humidity.

Deeper soil layer profiles of 2–4 cm and 4–6 cm contribute substantially to VOX production, but data is not shown here due to the early stage of supervision. However, based on the 0–2 cm data a productive day in 2008 could have led to the notable

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emission up to 23 t dichloroethene within the research area of 15 000 km^2. This number will be increased when applying the method to the remaining salt affected soils of the 50 000 km^2 ranging Aralkum and the surrounding salt affected soils.

Expanding the production time to the whole spring season, with its high temperatures but still moist soil system, can theoretically end in production of several thousand tons of DCE towards the beginning of wintertime.

Furthermore, referring to earlier findings of elevated VOX production in hyper-saline sediments of halite precipitating lake systems (Weissflog et al., 2005) the emission load may increase dramatically if the emission data for the remaining hyper-saline water body of the Aral Sea can be included.

Including emission data of the deeper soil layers will further top up the overall production.

Since DCE is only one agent for a range of chemical substances, the total VOX emission loads can easily increase exponentially when including other halogenated organic compounds.

To stress the global relevance of hyper-saline environments as natural VOX sources typical emission data from saline sediments in southern and northern Africa, as well as southern Russia and middle Asia are combined in Table 3.

Saline sediments at the Namibian coastline as well as the Makgadikgadi salt flats in central Botswana outrange the DCE production of the former sediments of Aral Sea. Halogenated C1-compounds like $CHCl_3$ and $CHBr_3$ occur consistently (also reported by Weissflog et al., 2005), whereas others seem to be specific to one location – e.g. $CHBr_2Cl$ for Botswana.

Interestingly VOX emissions such as CH_3Cl and CH_3Br were also found under dry condition. The underlying production scheme might have similarities to the pectin hydrolysis reported by Wishkermann et al. (2008) and suggests a degradation of plant material – e.g. algae mats – that remain in the topsoil during dry season.

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Including these findings an efficient VOX production is no longer bound to rain events and flooding, in fact a VOX emission throughout the whole year becomes likely, particularly for southern African saline ecosystems.

4 Conclusions

The main question is: How can VOX emission be extrapolated from small-scale soil measurements to landscape scale? Synergistic use of VOX emission data and remote sensing products have first been proven to be a suitable approach for estimating the VOX production in saline ecosystems as well as extrapolation of field measurements to larger scales. The applied setup reproduces a short-term change in climatic conditions starting from dried-out saline soil, instantly humidified during rain events or flooding. Considering halide concentrations (Cl^-, Br^-) as one of the major driving forces to VOX emission, a future scenario of increased VOX emission becomes likely for Central Asia and particularly for the Aralkum.

But at this stage the applied method still contains large uncertainties regarding the accuracies of land cover classification with focus on salt composition and soil humidity. Several salt types show different spectral profiles (Fig. 5), which can be measured by means of remote sensing data (Ben-Dor et al., 2002; Hunt et al., 1972). Highly saline soils can be distinguished from low or even non-saline soils as reported by Metternich and Zinck, (2003 and 2009). But, since the emission of VOX is mainly connected to surface salt composition, a higher level of detail is needed to calculate the soil classes with sufficient accuracy.

The future challenge is to detect rapid changes in surface composition and land cover of saline environments, with adequate precision and at different temporal and spatial scales (e.g. salt type, dissolving and re-crystallization following rain events). This includes evaluating the capacity of hyper spectral data to discriminate saline ecosystem surface components (soil, salt types, and vegetation). In order to enhance understanding of small-scale surface heterogeneities and their influence on regional VOX emission

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rates, a multi-scale classification system has to be implemented, including sensors with different spatial and temporal resolution.

Future purposes are: (i) to quantify VOX emission from saline ecosystems and to determine their driving environmental parameters; (ii) spatial extrapolation of these environmental parameters through classification of different salt types (e.g. sulphate versus halide) and of small-scale surface heterogeneities; (iii) to extrapolate these parameters to larger scales using remote sensing and to verify rapid changing climate condition; (iv) to assess spatial and temporal variability as baseline information for; (v) modelling of landscape evolution and VOX emission budgets.

A combination of data from field surveying, laboratory analysis and remote sensing has to be used in future studies. Information on VOX emission will be obtained from field surveys and subsequent laboratory analysis. Spectroscopic data will be obtained with a field spectrometer during field campaigns, whereas site-specific libraries will be created. The libraries will contain spectral information for the most representative surface components combined with soil sample analysis (e.g. pH and chemical composition), vegetation classification, and topographic and meteorological data. A possible methodological procedure is summarized in Fig. 6.

Critical steps can be expected (i) when correlating environmental parameters with VOX emission and (ii) when assigning VOX emission to distinct land cover classes, which are directly or indirectly influenced by these parameters and distinguishable by means of remote sensing. A final step would be monitoring of past and future landscape evolution, including rapid change assessment, and modelling of VOX emission. This would allow for spatial and temporal quantification of VOX emitted from whole saline ecosystems e.g. the spreading Aralkum desert in Central Asia.

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Table 1. Matrix of land cover change derived from MODIS time series classification. Area statistics for 2000, 2004 and 2008.

Land cover class		2000		2004		2008	
Typ	Description	[km^2]	[%]	[km^2]	[%]	[km^2]	[%]
Shrubland	Mainly shrubs (e.g. *Haloxylon aphyllum, Tamarix sp.*), vegetation coverage > 15 %	4493	30.1	3828	25.6	5649	37.8
Reed	Reeds, mainly dominated by Phragmites sp., partly with other vegetation (mostly shrubs)	2961	19.8	3891	26.0	1737	11.6
Bare Area	Bare soils and unconsolidated materials, sand sheets and dunes, soils with scattered vegetation, vegetation coverage < 15 %	2261	15.1	1974	13.2	3024	20.2
Salt Soil	Salt affected soils (e.g. Solonchaks, Takyrs)	2014	13.5	3036	20.3	3707	24.8
Salt Crust	Salt crusts surrounding Aral Sea shoreline	320	2.2	695	4.7	717	4.8
Water	Shallow lakes, reservoirs and the Aral Sea	2888	19.3	1514	10.1	105	0.7
Total		14 940	100	14 940	100	14 940	100

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Table 2. Estimated dichloroethene production for the 15 000 km^2 ranging research area, based on 0–2 cm soil profile data. DCE production within 24 h under the favourable condition of a moist soil system and 25–35 °C air temperature. Concentrations are given for each land cover class in kg DCE/covered area.

Land cover class and corresponding site		DCE production [g km^{-2}]	Land cover area per class [km^2]			DCE production [kg/land cover area]		
			2000	2004	2008	2000	2004	2008
Shrubland	T9	1004	4493	3828	5649	4511*	3843*	5672*
	T11	2703				12 144**	10 347**	15 269**
Reed	no site	n.d.	2961	3891	1737	n.d.***	n.d.***	n.d.***
Bare Area	T1	991	2261	1974	3024	2241**	1956**	2997**
	T4	889				2010*	1755*	2688*
	T6	n.d.				n.d.***	n.d.***	n.d.***
Salt Soil	T5	1090	2014	3036	3707	2196	3310	4042
	T7	n.d.				n.d.***	n.d.***	n.d.***
	T10	n.d.				n.d.***	n.d.***	n.d.***
Salt Crust	T3	915	320	695	717	293	636	656
Water	no site	n.d.	2888	1514	105	n.d.***	n.d.***	n.d.***
Sum high						16 873	16 249	22 963
Sum mid						9009	9544	13 057
Sum low						4803	4479	6327

* mid value, ** higher value, *** low value, n.d. = not detectable

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Table 3. Typical VOX emission characteristic of saline soils sediments of different origin using purge-and-trap GC/MS analysis. 24 h incubation time; moist or dry sediments – ongoing study [g m^{-2}].

VOX species		Uzbekistan Southern Aral Sea	South Russia Volgograd region	Namibia Walfishbay coastline	Botswana Makgadigkadi Pan
Chloromethane	CH_3Cl	–	15 240 *	14 410 *	–
Bromomethane	CH_3Br	–	1040 *	1160 *	–
Dichloroethene	$C_2H_2Cl_2$	2640	–	20 700	8270
Trichloromethane	$CHCl_3$	4640	1480	3620	2190
Trichloroethene	C_2HCl_3	290	–	–	1290
Dibromochloromethane	$CHBr_2Cl$	–	–	–	9800
Tetrachloroethene	C_2Cl_4	–	–	430	360
Tribromomethane	$CHBr_3$	380	2570 *	–	–

*only detected under dry condition.

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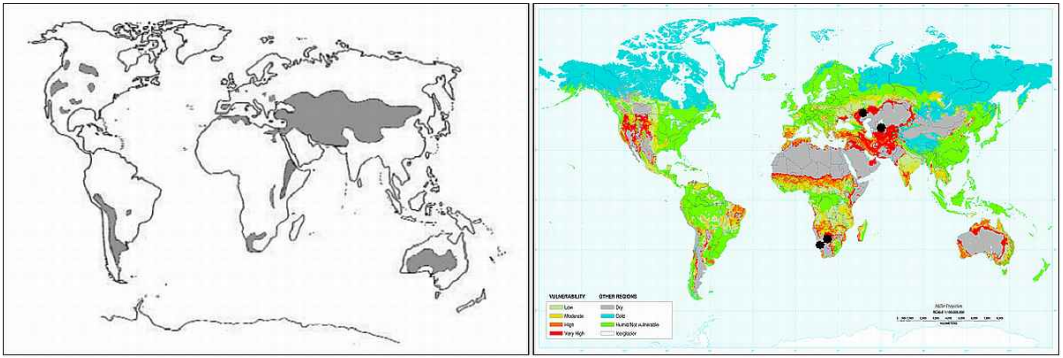

Fig. 1. Left: Global distribution of recent salt lakes and salt soils (Williams, 2002). Right: Global desertification vulnerability (USDA-NRCS, Soil Survey Division, World Soil Resources, Washington D.C. 1996). Black dots indicate the study areas mentioned in this study: Aralkum desert in Central Asia, Kalmykia in southern Russia, coastal wetlands of Namibia, and inland salt flats of Botswana.

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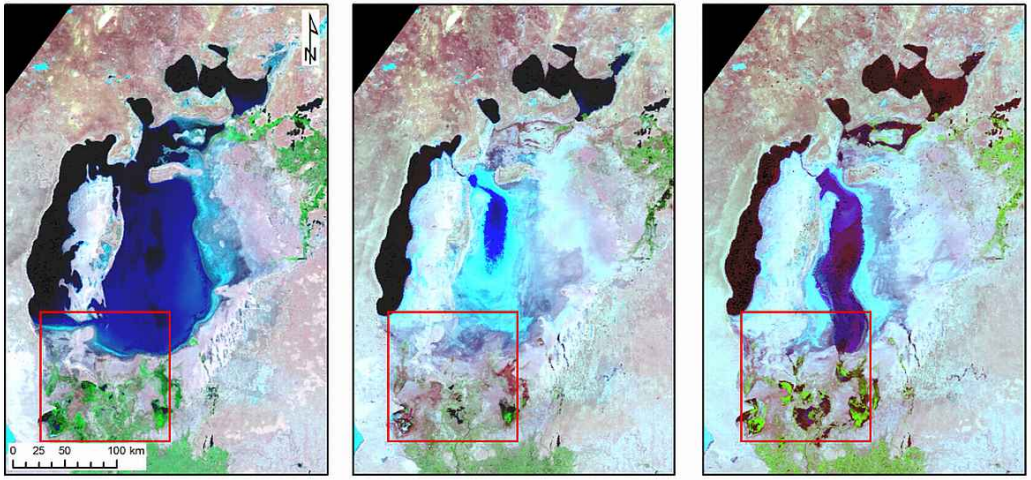

Fig. 2. Highly dynamic, spreading saline ecosystem: the Aralkum in Central Asia. Terra MODIS images acquired on July 2000, 2009 and 2010. Images displayed in false color band combination 7-2-1. Red squares indicate the study area.

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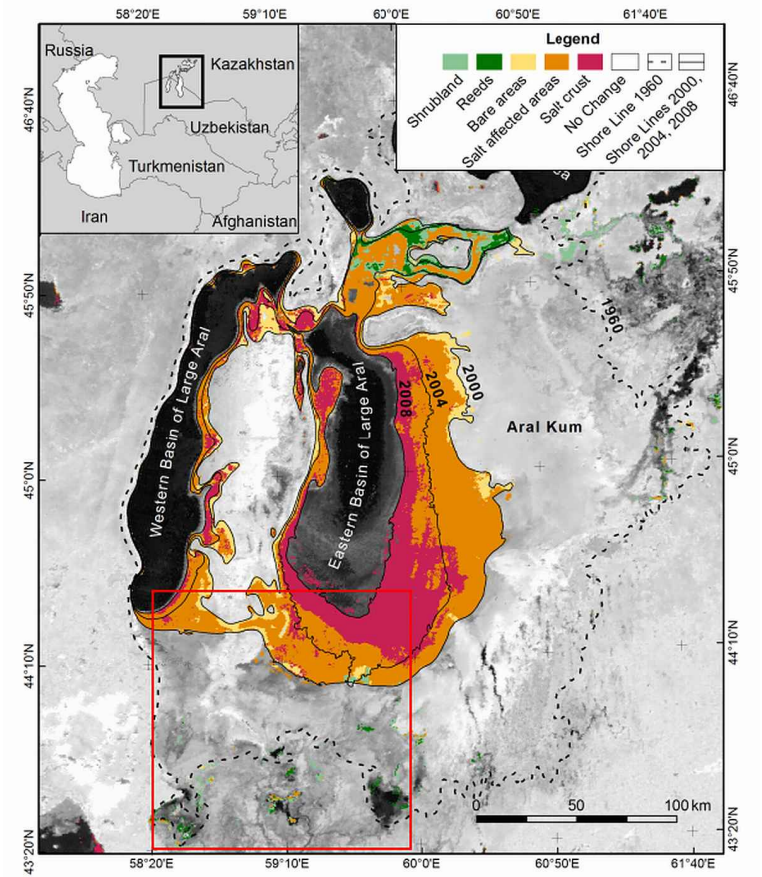

Fig. 3. Location of the study area in the southern Aral Sea Basin. The map shows the major land cover transformations that took place where the sea surface has desiccated between 2000 and 2008. The image backdrop is a Terra MODIS scene acquired on July 2009, Julian calendar day 201. Red square indicates the study area.

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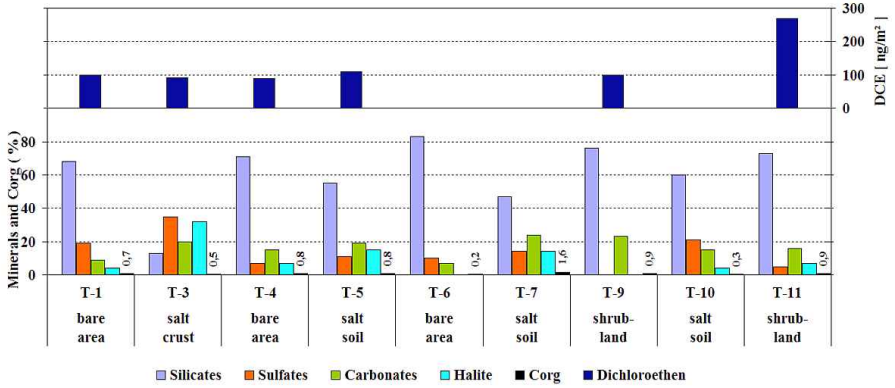

Fig. 4. Mineral content and C_{org} versus dichloroethene (DCE) production. Samples of topsoil layer 0–2 cm (including crusts), incubated for 24 h after adding water. DCE determination by purge & trap headspace GC-MS. Concentrations given in [ng m^{-2}]. Land cover classes of location T1 till T11 are classified through MODIS time series analysis (see Table 1). C_{org} values are given as numbers additionally.

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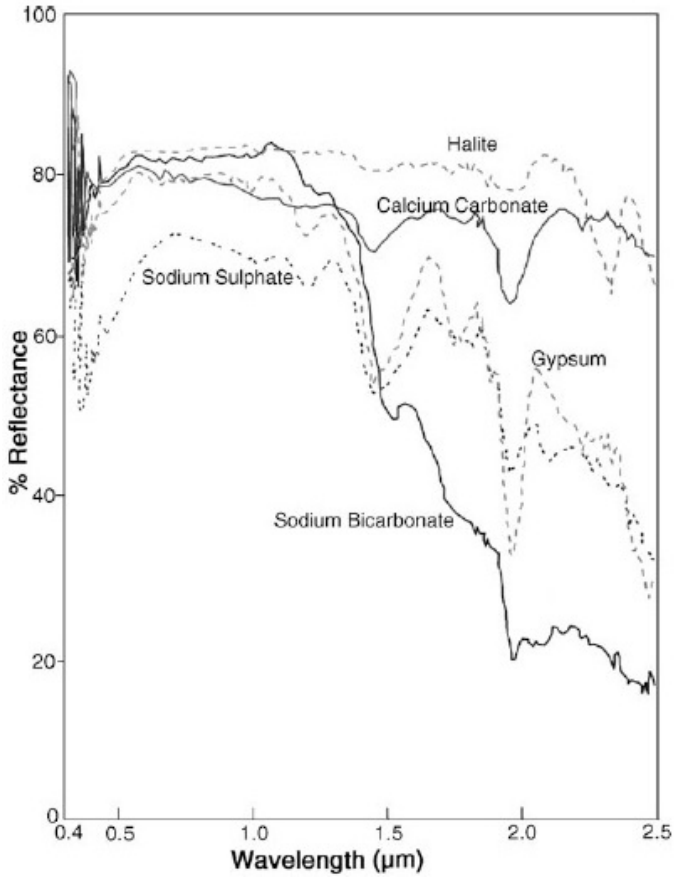

Fig. 5. Spectral profiles of gypsum, halite, calcium carbonate, sodium bicarbonate, and sodium sulphate in the visible, near, and mid-infrared (0.4–2.5 μm), as recorded by the GER 3700 spectroradiometer. Source: Metternich and Zinck (2003).

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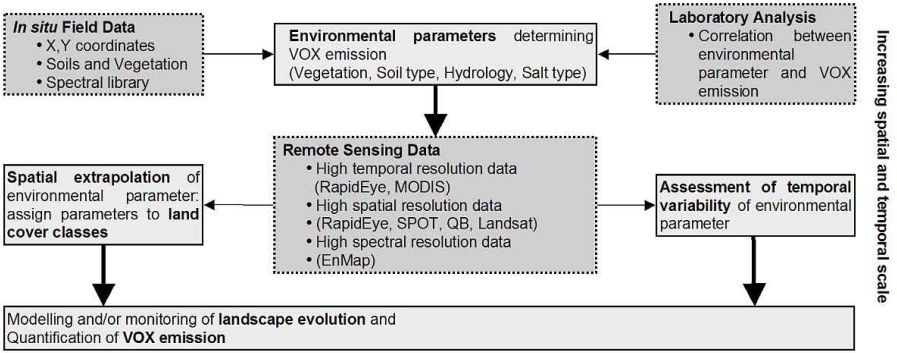

Fig. 6. Proposed workflow for extrapolation of VOX emission from soil measurements to larger scales.

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