

Influence of altitude concerning the contamination of humus soils in the German Alps: a data evaluation approach using PyHasse

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Abstract

Background, aim and scope In an international project named MONARPOP (Monitoring Network in the Alpine Region for Persistent and other Organic Pollutants), selected chemicals in different environmental media were analysed in the years 2004 and 2005. Seventeen pesticides were chosen and analysed in humus and mineral soil in the German Alps. The samples were taken at different altitudes. **Materials and methods** In such a rather complex environmental datasets, it is often necessary to compare different sets of criteria and their influence on rankings. In the similarity analysis which is part of the theory of the Hasse diagram technique, we intend to calculate the similarity of different rankings. Furthermore, we perform a so-called dominance–dominance/dominance–separability method, followed by a sensitivity analysis, both subroutines in the newly developed PyHasse programme in order to find out if the concentration of the chemicals can be related to the altitudes at which the samples were taken.

Results and discussion It can be demonstrated that the altitude has a considerable influence on the concentration of some organic chemicals in humus: The concentrations of some chemicals increase with the altitude. This increase shows certain irregularities for which several explication attempts including possible effects of atmospheric stratification phenomena in valleys have been made.

Conclusion These results should be complemented in further studies with MONARPOP monitoring data from other Alpine countries, e.g. Austria, Switzerland, Italy and Slovenia.

Keywords Hasse diagram technique · PyHasse · Dominance–dominance/dominance–separability method · Ranking method · Pesticides · Meteorology · Alps

1 Introduction: pesticides found in the Alps

A huge amount of data was generated during the international project named MONARPOP (Monitoring Network in the Alpine Region for Persistent and other Organic Pollutants). Selected chemicals in environmental media in the mountain area of the Alps were analysed in the years 2004 and 2005 (MONARPOP 2008). Seventeen pesticides (see Table 1) were chosen and monitored in soil samples in Germany, Austria, Switzerland, Italy and Slovenia. The samples were taken from different matrices and altitudes. In this paper, we take a closer look at 11 humus (soil) samples from different altitudes in the Bavarian Alps (Germany). Our aim was to get an idea if altitude of the sampling site has an influence on the concentration of chemicals of highly different physico-chemical properties and biodegradation rates.

Most of the chosen chemicals belong to the group of persistent organic pollutants (POPs). These chemicals,

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Table 1 Pesticides analysed (name, acronym, CAS number)

Number	Name	Trivial name	Acronym	CAS number
01	alpha-Hexachlorcyclohexane	alpha-HCH	AHCH	319-84-6
02	beta-Hexachlorcyclohexane	beta-HCH	BHCH	319-85-7
03	gamma-Hexachlorcyclohexane	gamma-HCH	GHCH	58-89-9
04	delta-Hexachlorcyclohexane	delta-HCH	DHCH	319-86-8
05	epsilon-Hexachlorcyclohexane	epsilon-HCH	EHCH	6108-10-7
06	<i>p,p'</i> -Dichlordiphenyltrichlorethane	<i>p,p'</i> -DDT	PPDT	50-29-3
07	<i>o,p'</i> -Dichlordiphenyltrichlorethane	<i>o,p'</i> -DDT	OPDT	789-02-6
08	<i>p,p'</i> -Dichlordiphenyldichlorethane	<i>p,p'</i> -DDD	PPDD	72-54-8
09	<i>o,p'</i> -Dichlordiphenyldichlorethane	<i>o,p'</i> -DDD	OPDD	53-19-0
10	<i>p,p'</i> -Dichlordiphenyldichlorethene	<i>p,p'</i> -DDE	PPDE	72-55-9
11	<i>o,p'</i> -Dichlordiphenyldichlorethene	<i>o,p'</i> -DDE	OPDE	3424-82-6
12	Aldrin	Aldrin	ALDR	309-00-2
13	Dieldrin	Dieldrin	DIEL	60-57-1
14	Endrin	Endrin	ENDR	72-20-8
15	Mirex	Mirex	MIRE	2385-85-5
16	Hexachlorobenzene	HCB	HCBE	118-74-1
17	Heptachlor	Heptachlor	HECL	76-44-8

known as ‘poisons without passports’, pose particular hazards because of their common effects: They are toxic to humans and wildlife. Additionally, they are persistent (and resist degradation). POPs are semivolatile and mobile, travelling long distances on wind and water currents and are widely distributed throughout the environment. Through global distillation, they travel from temperate and tropical regions to be deposited in the colder regions of the poles (IPEN 2005) or as demonstrated in the MONARPOP project in the Alps. In awareness of the immense damage these chemicals cause, the Stockholm Convention on Persistent Organic Pollutants was established and came into force in 2004. The objective of this convention (Stockholm Convention on Persistent Organic Pollutants) is to protect human health and the environment from POPs. Unlike other chemical treaties that rely primarily on notification requirements or end-of-life management controls, the POPs Convention aims at eliminating the production, use and emissions of POPs. It also aims to ensure the environmentally sound destruction of POPs waste stockpiles as well as to prevent the introduction of new chemicals with POP-like characteristics.

There is an urgent need to monitor these dangerous chemicals and furthermore to extract knowledge from the data by means of mathematical and statistical evaluation methods. It is evident that standard multivariate statistical methods, like principal component analysis, etc., will give more insight into the data. However, here, the evaluative aspect is our main focus; therefore, we present a ranking approach based on partial order theory and its software realisation by PyHasse. The background of this software will be briefly explained in Section 2.

First, we take a look at the chosen set of chemicals and locations (sites) where the samples were taken.

Table 1 lists the objects to be analysed; our interest refers to the group of pesticides.

Among the sites, we selected two altitudinal profiles, which consisted of five (transect Walchensee-Eschenlohe) resp. four (transect Berchtesgaden) plots and two additional sites. The selection of sites was performed in a standardised way, with restriction to sites in 80–120 years old spruce forests (*Picea abies* (L.) Karsten). Due to the highly complex orography, differences in geometry of the four slopes could not be avoided; slope exposition and inclination vary from one site to another. Therefore, we expect to obtain only meaningful rules by restricting our analysis to an ordinary scale. Table 2 lists these sites together with their plot identification numbers and their Hasse diagram technique identification numbers, their location, altitude and relief characteristics.

Hence, we initially come up with a 17 chemicals \times 11 detection sites data matrix. For our evaluation purposes concerning the importance of the altitude on the data analysis, we transpose the data matrix into a 11 \times 17 data matrix.

The question we want to answer is: Can we find out how chemicals’ concentrations vary with the altitudes and if there are exceptions which chemicals are causing these. In order to answer this question, we divide the altitude into five classes. Then, we apply the so-called dominance–dominance/separability (DDS) method, a subroutine in the PyHasse program recently developed by the second author. This methodology will be explained and applied in the following sections. It is clear that one may

Table 2 Plot IDs, their location and altitude (Germany, soil samples)

Number	Plot ID project	ID Hasse	Location	Region	Altitude (m)	Relief
01	DE-21-1	HD01	Walchensee-Eschenlohe	Werdenfels Alps	830	Flat SE-facing slope
02	DE-21-2	HD02	Walchensee-Eschenlohe	Werdenfels Alps	1,030	Steep N-facing slope
03	DE-21-3	HD03	Eschenlohe	Werdenfels Alps	1,230	Flat N-facing slope
04	DE-21-4	HD04	Eschenlohe	Werdenfels Alps	1,450	Flat mountain ridge
05	DE-21-5	HD05	Eschenlohe	Werdenfels Alps	1,650	Steep S-facing slope
06	DE-22-0	HD06	Kiefersfelden	Inntal Alps	1,405	Flat N-facing slope
07	DE-23-1	HD07	Berchtesgaden	Berchtesgaden Alps.	805	Steep N-facing slope
08	DE-23-2	HD08	Berchtesgaden	Berchtesgaden Alps	1,005	Flat W-facing slope
09	DE-23-3	HD09	Berchtesgaden	Berchtesgaden Alps	1,210	Flat N-facing slope
10	DE-23-4	HD10	Berchtesgaden	Berchtesgaden Alps	1,420	Flat SE-facing slope
11	DE-20-0	HD11	Sonthofen	Allgäu Alps	1,405	Flat NW-faced slope

HD humus soil, DE Germany

think on basic (typical) statistical measures like mean and median to characterise the subsets. However, we prefer a parameter-free approach corresponding to our ordinal approach, aiming at a ranking.

2 Methodology: DDS–domination–domination–separability, a subroutine of PyHasse

Partial order is a discipline of discrete mathematics, and one may consider partial order as an example of mathematics without arithmetic. A good overview can be found in books edited by the second author (Brüggemann et al. 2001; Brüggemann and Carlsen 2006). The graphical representation of partial orders is laid down in so-called Hasse diagrams. We consider Hasse diagrams as a visualisation of a ‘generalised’ ranking. ‘Generalised’, as it is possible—and accepted—that not all objects are mutually comparable.

Whether or not objects are comparable depends on the data characterising them. Consider three objects *a*, *b* and *c* which are characterised by two attributes. Let now object *a* have the attribute values 2 and 5, *b* the values 6 and 6 and *c* the values 1 and 7. Then, object *a* is comparable to *b* because all values of *a* are simultaneously less than those of *b*. However, object *a* is incomparable with object *c* because the first attribute value is smaller but the second one is larger than the corresponding ones of *c*. Similarly, *b* is incomparable with *c*. See for details Brüggemann et al. 2001.

In our case, the objects are altitudes which are characterised by chemicals’ concentrations. Hence, different altitudes will not necessarily be comparable because we have to check several chemicals’ concentrations simultaneously.

In complex environmental datasets, it is often necessary to compare different sets of criteria (attributes). In the

similarity analysis, we intend to calculate the similarity of different generalised rankings. This similarity analysis is an important feature of the newly developed software package called PyHasse. PyHasse comprises currently 23 modules, elaborated by the second author and is still under development. Test versions are, however, available from Rainer Brüggemann (Brüggemann and Voigt 2008; Voigt et al. 2008a, b).

The dominance degree or domination–domination–separability (later only referred to as DDS) is a module in the PyHasse software. The basics of the dominance degree approach were published by Restrepo et al. (2008) and can briefly be explained as follows: A set of substances *G* may be partitioned into several “classes” which can be found either by unsupervised classifications, such as cluster analysis, or in a supervised manner. The question is whether it is possible to rank such classes. Ranking can be based on standard statistics, for example, medians or means. Nevertheless, the order theoretical approach of dominance degree (Restrepo et al. 2007) is preferable because it extends the parameter-free method of Hasse diagram technique. Two disjoint classes (subsets) *G_n* and *G_m* in *G* are formed, of which *G_n* completely dominates *G_m* if for all *x* in *G_n* and for all *y* in *G_m* $x \geq y$.

An example will be helpful (Fig. 1).

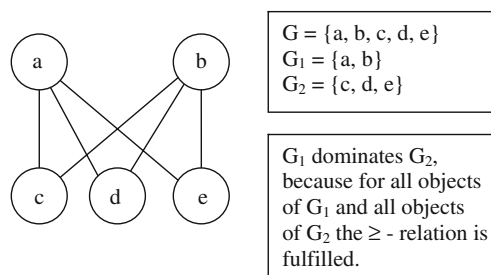


Fig. 1 Example for *G₁* dominating *G₂*

The condition “for all” implies that all objects in G_n are ranked higher than those in G_m (see Fig. 1 where G_1 is ranked higher than G_2). In practice, this is not always the case because it often occurs that some objects of G_n and G_m are incomparable, or some objects in G_n may be ranked higher than those in G_m whilst some others are lower. Hence, it is necessary to quantify how many objects in G_n are ranked higher than those in G_m ; this dominance of G_n over G_m determines the dominance degree.

As is known, the resulting digraph is not necessarily a partial order (see Restrepo and Brüggemann 2008); therefore, the term ‘dominance’ instead of order relation is used.

The dominance degree is derived as follows:

Given two subsets X_i and X_j , we define:

$$\text{Dom}(i,j) = |\{(x,y) \text{ with } x > y \text{ and } x \in X_i, y \in X_j\}|/N_{\text{Rel}} \quad (1)$$

$$\text{Sep}(i,j) = |\{(x,y) \text{ with } x||y \text{ and } x \in X_i, y \in X_j\}|/N_{\text{Rel}} \quad (2)$$

$$N_{\text{Rel}} = |X_i| * |X_j|. \quad (3)$$

It can be shown that the following equation holds (Restrepo et al. 2008):

$$\text{Dom}(i,j) + \text{Dom}(j,i) + \text{Sep}(i,j) = 1. \quad (4)$$

If the dominance values are low compared to all possible relations between two subsets, then we consider this as ‘noise’, i.e. non-relevant because the relations are mainly incomparabilities and there is no definite number of order relations of $x \in X_i$ over $y \in X_j$ or vice versa. A test statistics to quantify ‘non-relevant’ is to our knowledge not applicable; first approaches to tackle this problem can be found in Klukowski (2008). Therefore, we arbitrarily introduce a filter ε to decide when a relation between two subsets is considered as existing or not. If $\text{Dom}(i,j) > \varepsilon$, the subset i dominates subset j . One may consider this procedure as a kind of “defuzzification”. However, there is a deeper aspect behind “filtering”: As shown in Restrepo and Brüggemann 2008, a partial order relation can only be established for $\varepsilon > 0.5$

In the case shown in Fig. 2, there are many relations among the five subsets where a dominance cannot be established and few pairs of subsets, like subsets 1 and 3, where a dominance may be established tentatively. To find out these more distinct dominances, the dominance matrix $\text{Dom}(i,j)$ is scanned as follows: If $\text{Dom}(i,j)$ is greater than the filter value, then a relation is assumed.

If we write for a dominance relation “ \succ ”, then Fig. 1 shows:

- subset 1 \succ subset 0
- subset 1 \succ subset 2.

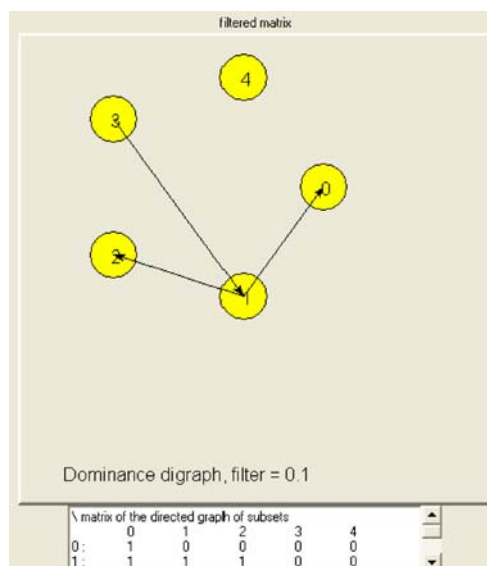


Fig. 2 Filtered matrix: dominance digraph, filter=0, 1 based on 17 chemicals and five altitude classes, namely subset 0 to subset 4

However,

subset 3 \succ subset 1.

Because subset 3 \succ subset 1 is not in accordance with the other two dominance relations and because of many missing relations in Fig. 2, we conclude that specific dominance relations according to the different altitude cannot be identified.

This negative result may be induced by the many incomparabilities found for the data matrix based on 17 chemical concentrations.

Therefore, we follow a stepwise strategy to find out chemicals which (1) induce the incomparabilities and (2) try to construct a data matrix whose sample points may obey an altitude relationship in a better way by eliminating chemicals.

The strategy is demonstrated in Fig. 2 where the concentrations of fictitious chemicals are shown as a function of altitude.

Figure 3 shows that for the fictitious chemical C3, the concentration decreases with altitude, whereas the other chemical concentrations increase, to a different extent, with altitude.

A Hasse diagram in which the samples (i.e. different altitudes) are the objects and the attributes are the chemical concentrations will be a complete anti-chain because C3 is anti-correlated to at least one other chemical, namely C1.

If C3 is eliminated, then the following Hasse diagram results (Fig. 4).

The order relations are almost (exception: Hmx||Hmd) following the altitude relation. If samples Hmx and Hmd would be put to one subset, Hl and Hfl to two other subsets,

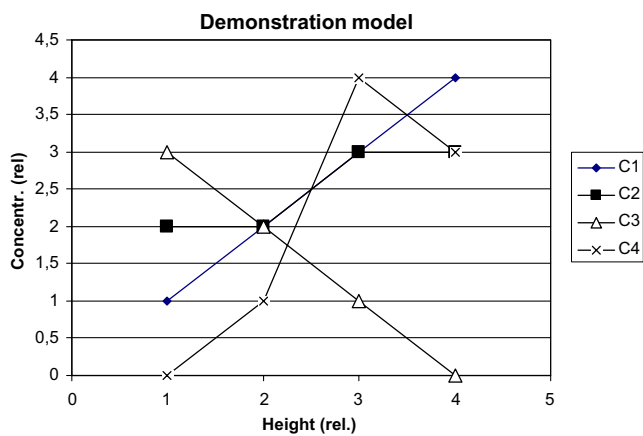


Fig. 3 Concentrations as a function of altitude for four fictitious chemicals

then the dominance digraph would show a clear dependence on altitude (as influencing factor; Fig. 5).

3 Applying DDS and sensitivity analysis to 11 different humus soil sample sites in the Alps eliminating chemicals in a consecutive way

A stepwise procedure is elaborated in order to find out more about the influence of the altitude on the detection of chemicals in the Alpine region in Germany followed by a sensitivity analysis (see Brüggemann et al. 2001). This procedure is given in Table 3.

3.1 Initial dataset: 11 humus soil samples × 17 pesticides

The samples of humus soil were taken at different locations and altitudes. From these different locations, we created the following five subsets which we name subset 0 through subset 4.

Five subsets were created according to the altitude and are listed in Table 4.

According to the theoretical example given in Section 2, we start calculating the dominance degrees followed by a

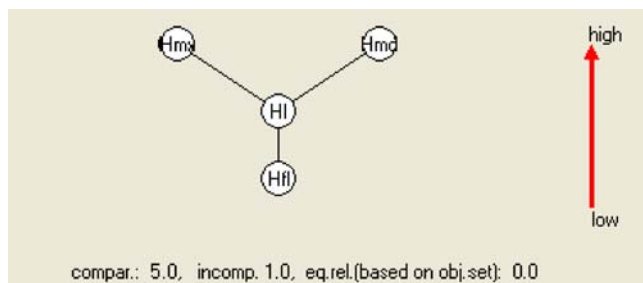
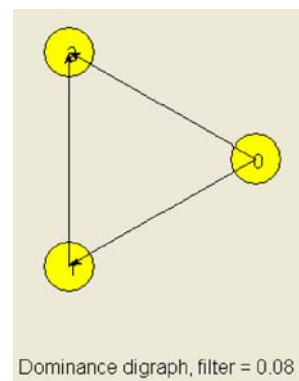


Fig. 4 Hasse diagram of samples (Hmx (altitude = 4), Hmd (altitude = 3), HI (altitude = 2) and Hfl (altitude = 1)) based on only three fictitious chemicals

Fig. 5 The digraph taken from the model system shows a total order: $0(\text{altitude : high}) > 1(\text{altitude : medium}) > 2(\text{altitude : low})$



filter process. The result is called a “filtered matrix” of the dataset. In Fig. 6A, a histogram of the frequency of the different dominance degrees of this 11×17 data-matrix is shown.

As we want to unify the procedure and in the end compare results, we always perform the dominance filter analysis with the value of 0.5. At this early stage, we are aware that no dominance is given at the value of 0.5, as can be seen in Fig. 5 and after applying filter $\epsilon=0.5$ in Fig. 7.

All five subsets are isolated. In the following procedure, we want to find out which chemicals have the highest impact on the order relation. To achieve this, we apply the sensitivity analysis, another feature of PyHasse (see Brüggemann et al. 2008) to the 11×17 data matrix. The results shown in the sensitivity vector define the concentrations of the chemicals PPDD and ALDR to be the most important attributes because they have the largest impact on all order relations. The data matrix is now reduced by these two chemicals. This means that we now have to cope with a 11×15 data matrix.

3.2 Step: DDS analysis with the 11×15 data matrix

With this reduced data matrix (11×15), the above procedure above is repeated.

A slightly better situation than in Fig. 6A (11×17) is encountered now in Fig. 6B.

The corresponding dominance digraphs for filters 0.2, 0.3, 0.4 and 0.5 are given in Fig. 8.

Due to Eq. 1, we have not only to consider the dominance but also the separability values. Hence, the limiting value of 0.2 is at best valid only for hypothesising: It may be correct that some chemicals follow the order given by altitude. However, as for instance $\text{dom}(i,j)=0.2$, the two other values $\text{dom}(j,i)$ and $\text{sep}(i,j)$ may vary in the range [0.2, 1]. Thus, not only incomparabilities but even countercurrent dominance relations may occur if such a low value is taken. Therefore, the strategy should be continued, applying filters of 0.5 and other values.

The sensitivity analysis applied to the 11×15 data matrix reveals that the attribute HECL is of great influence on the

Table 3 Stepwise procedure of DSS and sensitivity analysis

Data matrix	Step	Chemicals eliminated most influencing the partial order
11×17	Step 0	none
11×15	Step 1	PPDD, ALDR
11×14	Step 2	HECL
11×13	Step 3	OPDD
11×12	Step 4	AHCH
11×11	Step 5	GHCH
11×6	Step 6	DHCH, EHCH, PPDT, OPDT, HCBE
11×5	Step 7	BHCH
11×4	Step 8	ENDR
11×3	Step 9	PPDE
11×2	Step 10	OPDE
11×1	Step 11a	MIRE
11×1	Step 11b	DIEL

structure of the Hasse diagram (as the HD mainly consists of incomparabilities, the omission of HECL will enhance the number of comparabilities and therefore improve insight into the interaction between altitude and chemical concentrations).

3.3 Step: DDS analysis with the 11×14 data matrix

As can be expected, the number of dominances with high values is increased (see Fig. 6C).

A considerably better situation is encountered now. The filter process with 0.5 reveals the results given in Fig. 9.

Subset 4 (highest altitude) dominates subset 3, which dominates subset 2 in a linear order. Subset 4 dominates subset 1 as well as subset 0; subset 1 dominates subset 0.

This proves that the altitude has a considerable influence on the concentration of some organic chemicals in humus: The concentrations increase with the altitude.

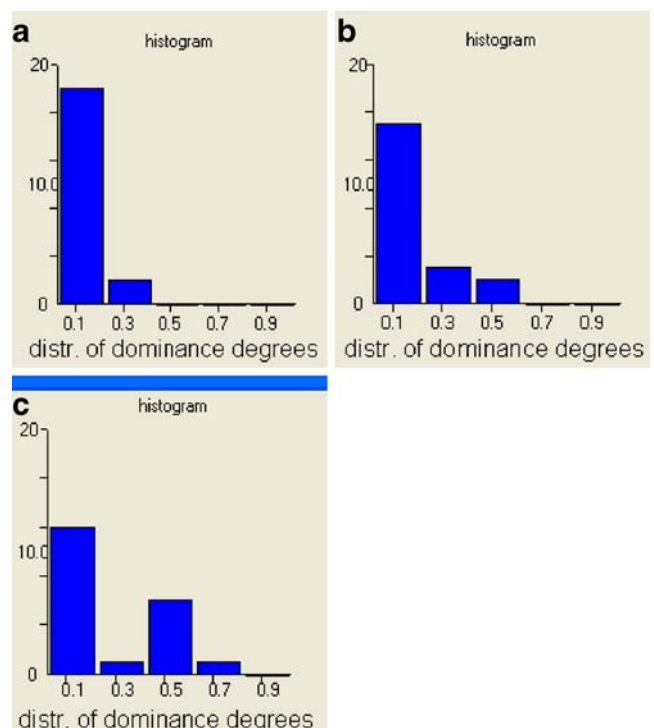
Table 4 Subsets of altitude

Altitude class (subset no.)	ID Hasse	Altitude (m.a.s.l.)
0	HD01	830
	HD07	805
1	HD02	1,030
	HD08	1,005
2	HD03	1,230
	HD09	1,210
3	HD06	1,405
	HD10	1,420
	HD11	1,405
4	HD04	1,450
	HD05	1,650

m.a.s.l. metre above sea level

Now we know the general influence of altitude on the chemical concentrations. There may be chemicals which evidently follow this qualitative behaviour, but there may also exist chemicals reacting specifically on cofactors-related altitude.

Sites of different altitude are characterised mainly by different meteorological parameters, which have a strong impact on mountain ecosystem dynamics, e.g. the abundance of (singular) species; additionally, many factors governing the behaviour of pollutants, for instance the

**Fig. 6** Histogram: distribution of dominance degrees A (11×17 DM), B (11×15 DM), C (11×14 DM)

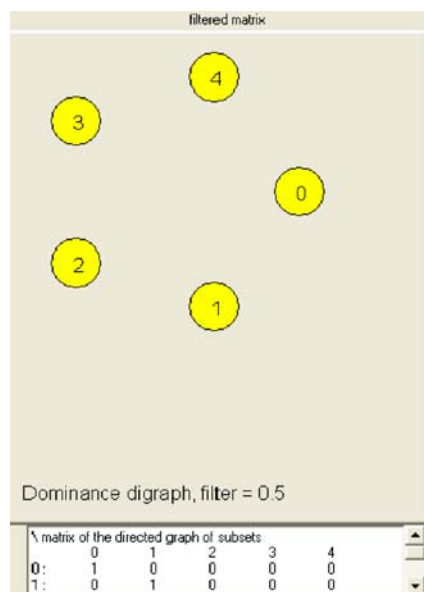


Fig. 7 Filtered matrix: dominance digraph, filter = 0.5 (11 × 17 DM)

deposition and decomposition, depend on local climate. In the framework of MONARPOP project, we estimated for each site annual temperature and precipitation using data from adjacent meteorological stations. On the basis of annual values (1960–1990), vertical temperature decrease ranges between -0.5°C and $-0.4^{\circ}\text{C}/100\text{ m}$ ($r^2 > 0.95$) in the Northern Alps, whereas precipitation increases between 25 and 28 mm/100 m ($r^2 > 0.86$; MONARPOP 2008). However, local effects caused by the relief were not taken into consideration. Therefore, ‘persistent cool-air pools’ and the formation of temperature inversions (Savov et al. 2002) disturb a completely homogeneous temperature decrease with altitude. The altitude and duration of such phenomena depend on valley geography and the characteristics of the slope. In general, both transects (Eschenlohe and Berchtesgaden) examined here are exposed to the north, but the first one is facing the rather flat foothills whereas the second is situated on the slope of a west/east-orientated valley. The ‘Sonthofen’ site is rather comparable to profile ‘Eschenlohe’; ‘Kiefersfelden’ site is located several kilometres from the northern margin of the Alps in a narrow valley.

In the following, we continue the sensitivity analysis, combined with the DDS approach in order to find groups of chemicals of similar behaviour. Instead of the commonly applied cluster analysis methodology, we maintain the ordinal context and apply order theoretical tools.

Sensitivity analysis of a 11×14 data matrix reveals that the attribute OPDD is of great influence on the structure of the Hasse diagram (as the HD mainly consists of incomparabilities caused by the attribute OPDD concentration, the omission of OPDD will enhance the number of comparabilities and therefore improve the insight into the interaction between altitude and chemical concentration.

3.4 Further steps: DDS analysis with reduced data matrices

The stepwise procedure including a reduction of the attributes (chemicals) will be performed until we only cope with one chemical (11×1 data matrix). The results are given in Table 3 (which chemicals are left out), and the dominance digraphs (filter=0.5) are shown in Fig. 10.

It is remarkable that during steps 6–10, no change in the dominance degree digraphs is detected. This means that the structure of the digraphs in Fig. 9 and the corresponding Hasse diagrams (Fig. 10) are very stable, and none of the remaining chemicals has an impact on the altitudinal order of observations. Drawing all the digraphs of Fig. 9 as Hasse diagrams (see Fig. 10), one can see that finally, almost a linear order among the altitude classes is obtained. Subsets 2 and 0 form an exception; because these two subsets are incomparable until step 10 and still worse, there is an inversion, namely subset 2 (representing approximately 1,200 m a.s.l.), appearing below subset 1 (representing the altitude class of 1,000 m a.s.l.).

Only among the altitude classes 4, 3, 1 and 0, a relationship exists when we take a look at the following six chemicals: BHCH, ENDR, PPDE, OPDE, MIRE and DIEL. The altitude class 2 is different from the other levels. In general, it could be demonstrated that all chosen altitude classes—with the exception of class 2—have a great influence on the concentrations of a selected and identified set of chemicals.

The altitude class 2 corresponds to a zone of 400–500 m above the valley floor or the adjacent lowlands. Despite a general vertical decrease of temperature, this level may, in some alpine regions, coincide with a relatively thin warm in the mid-slope. This zone with relatively high insolation lies above the frequently occurring cool-air pools and below the zone influenced by the large-scale atmospheric winds (Frenzel and Fischer 1957). Hence, it cannot be excluded that this so-called warm slope zone has an impact on deposition and degradation of POPs. Several other natural parameters which have not been registered or monitored in the framework of MONARPOP project may change along Alpine slopes too. Parameters which are related to the forest stand, leaf area index, carbon content in the humus, biodegradation activity are factors which can vary from plot to plot.

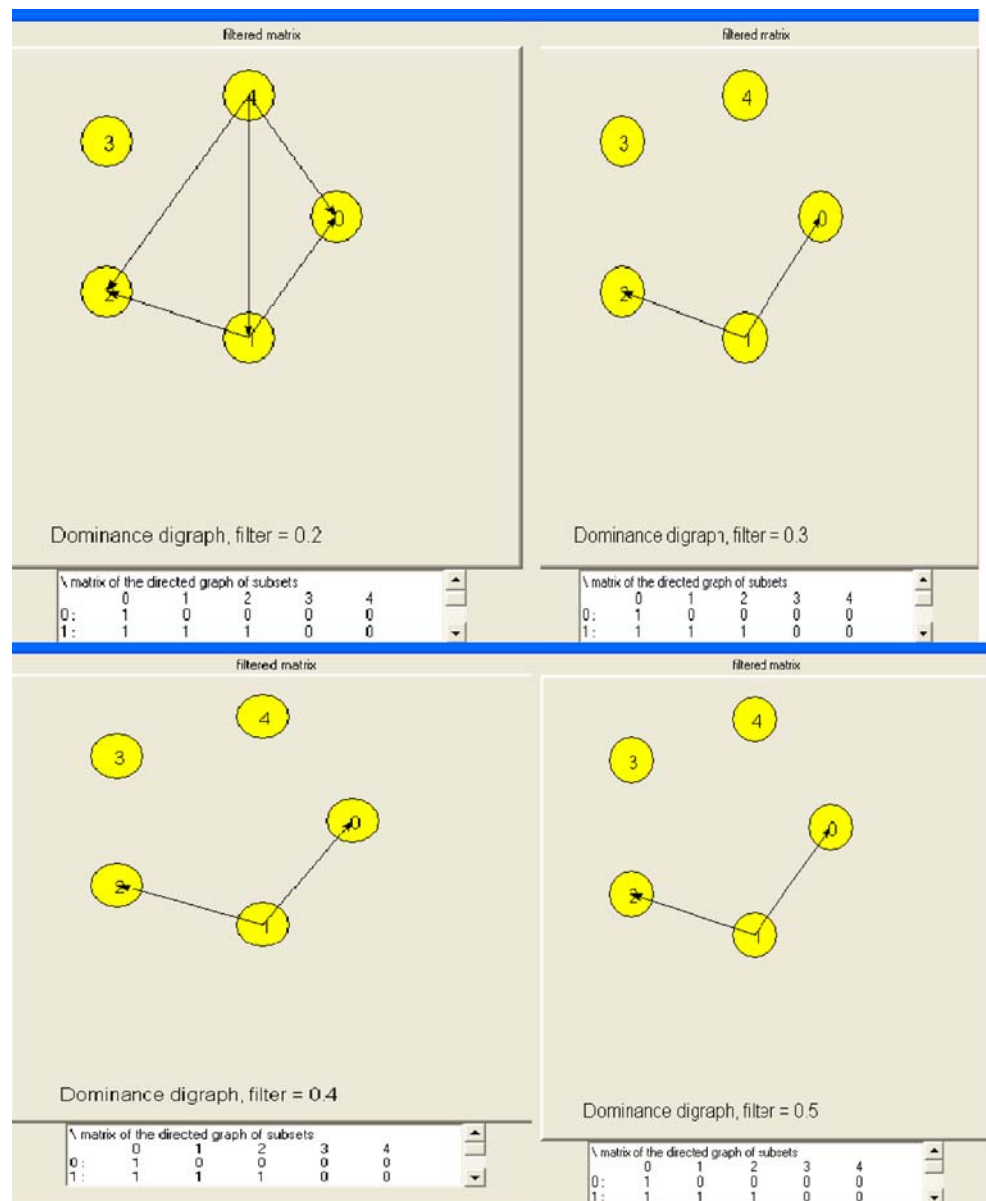
Further and more detailed knowledge might be gained from the data after calculation of Hasse diagrams for the shown dominance digraphs shown in Fig. 9.

3.5 Hasse diagrams for the calculated dominance digraphs

The Hasse diagrams for the stepwise chemical reduction procedure described in Section 3.4 are shown in Fig. 10.

The Hasse diagrams are shown in Fig. 11.

Fig. 8 Filtered matrix: dominance digraph, filter = 0.2, 0.3, 0.4, 0.5 (11 × 15 DM)



4 Discussion and outlook

These general results, i.e. of a vertical increase of some POPs, are supported by the findings for other altitudinal profile measurements performed in Austria and Switzerland gathered in the framework of the MONARPOP (2008) project as well as by other scientific studies and models. POPs are known to concentrate in cold environments as a result of progressive volatilisation from warm regions and condensation in colder areas. In addition to polar regions, high mountain areas are probably under probable stress from POPs (Villa et al. 2006). Weiss et al. (1998) and Blais et al. (1998) found higher accumulation of pesticides at higher altitudes along vertical profiles in Austria resp. North America higher accumulations of pesticides at higher

altitudes. Therefore, higher contamination of POPs in soils at higher levels results partly by higher deposition caused by higher precipitation rate and lower temperatures and partly by reduced degradation due to low temperatures. Wegmann et al. (2006) present first results of a modelling study to explore the occurrence and extent of cold condensation effects in mountains with the CliMoChem model for a group of POPs with different volatility and persistence. It is concluded that mountainous regions with lower temperatures than the surrounding lowlands and with increased precipitation rates may act as local cold condensers and may eventually become secondary emitters for a wide range of environmental contaminants.

It is therefore necessary to investigate the issue of organic pollutants in mountainous regions by means of

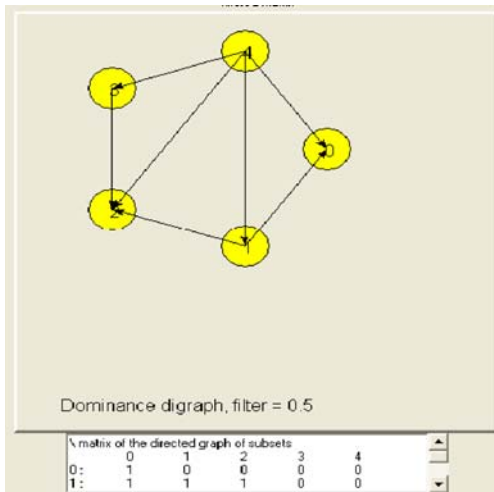


Fig. 9 Filtered matrix: dominance digraph, filter = 0.5 (11 × 14 DM)

carefully designed monitoring and modelling studies to encourage further investigations of the important processes in mountainous regions and to identify important parameters that control the occurrence and extent of cold condensation effects in mountain ranges. Recently, Daly and Wania (2005) addressed the issue of organic contaminants in mountains by reviewing the available literature on contaminants in various alpine media and identifying research needs. Among several points, they point out some chemical and environmental factors that control the concentration increase with altitude. Daly et al. (2007) described the distribution of organochlorine pesticides (OCP; in past and current use) in the mountains of western Canada by sampling air, soil, and lichen along three elevational transects in 2003–2004. Two transects west of the Continental Divide were located in Mount Revelstoke and Yoho National Park, whilst the Observation Peak

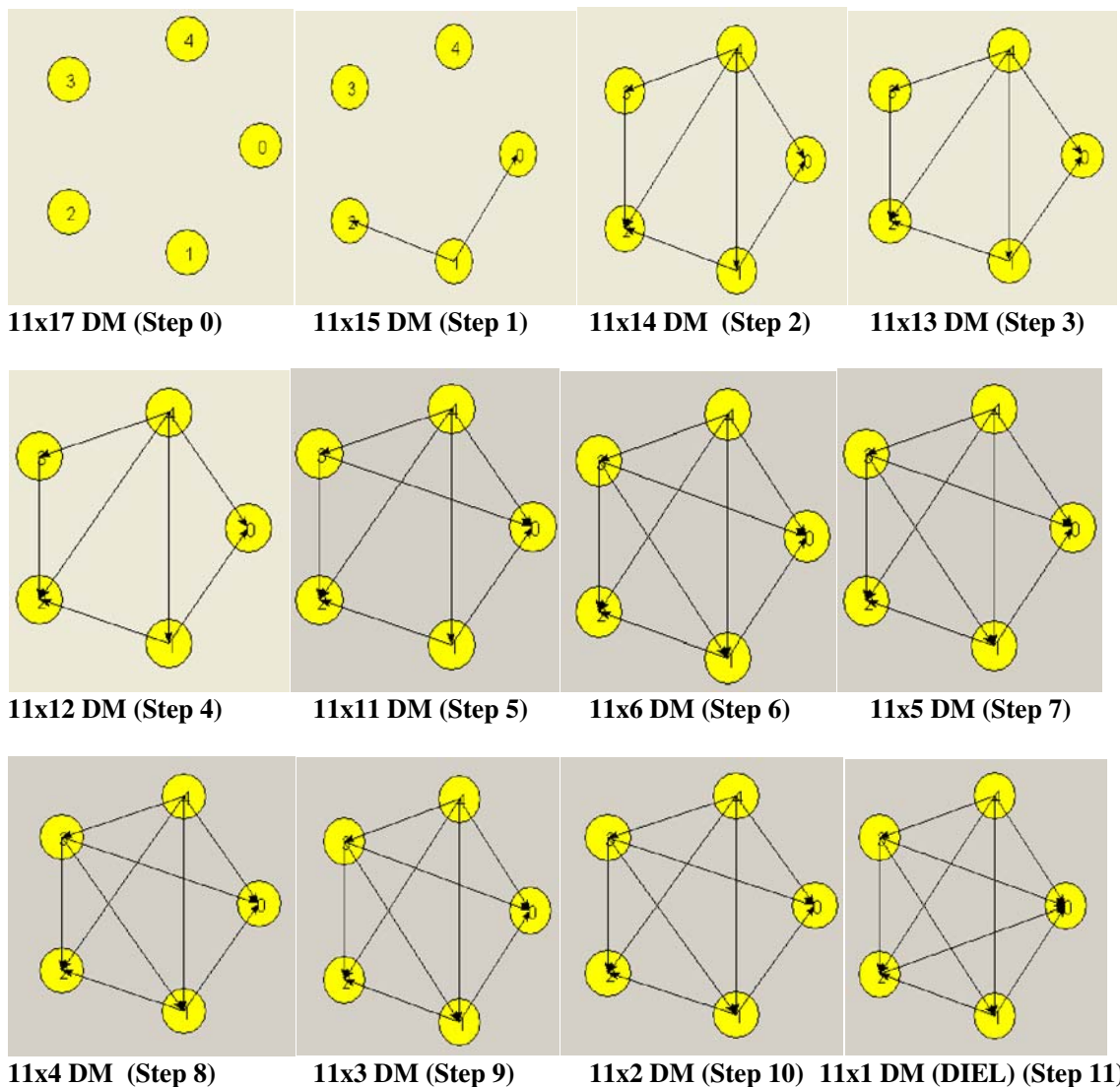
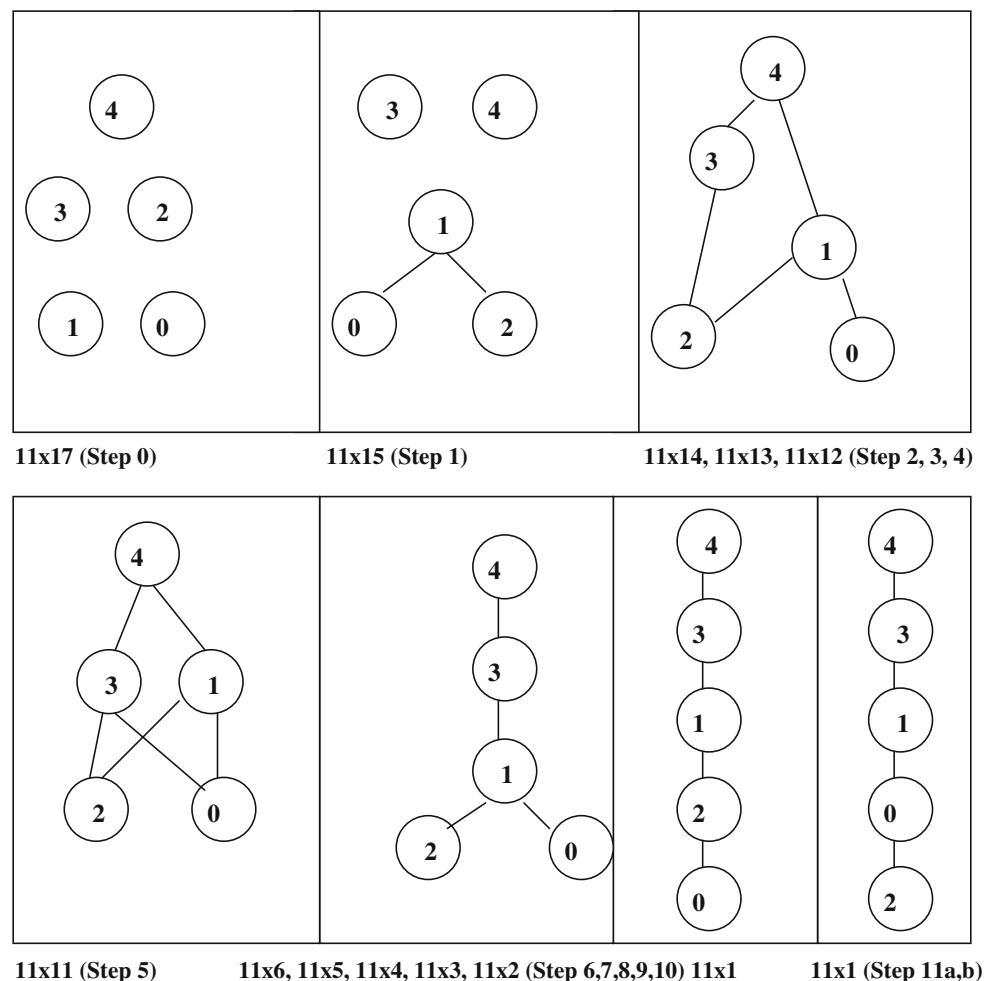


Fig. 10 Dominance digraph filter analysis in 12 steps (filter=0.5)

Fig. 11 Hasse diagrams of dominance digraphs

transect in Banff National Park is east of the divide. The soil and lichen concentrations of most OCPs increased with altitude in Revelstoke and displayed maxima at intermediate elevations at Yoho and Observation Peak. These distribution patterns can be understood as being determined by the balance between atmospheric deposition to and retention by the soils. Higher deposition, due to more precipitation falling at lower temperatures, likely occurs west of the divide and at higher elevations. Higher retention, due to higher soil organic matter content, is believed to occur in soils below the tree line. Highest pesticide concentrations are thus found in temperate mountain soils that are rich in organic matter and receive large amounts of cold precipitation.

Organochlorine chemicals (dichlorodiphenyltrichloroethanes, hexachlorocyclohexanes and hexachlorobenzene) were measured in ice melt water from five glaciers in the Italian Alps. Even though the data collected may not be sufficient for a precise description of POP release patterns from glacier melting, they have, however, highlighted the

potential for surface water contamination. Risk for the aquatic environment is excluded through direct water exposure, but it is likely to occur through biomagnification and secondary poisoning exposure (Villa et al. 2006).

Stocker et al (2007) modelled the effect of snow and ice on the global environmental fate and long-range transport potential of semi-volatile organic compounds. Snow and ice have been implemented in a global multimedia box model to investigate the influence of these media on the environmental fate and long-range transport of semi-volatile organic compounds. Investigated compounds included HCB, PCB28, PCB180, PBDE47, PBDE209, R-HCH and Dacthal. At low latitudes, snow acts as a transfer medium taking up chemicals from air and releasing them to water or soil during snowmelt. At high latitudes, snow and ice shield water, soil and vegetation from chemical deposition.

A PYTHON program allows a deepened graph theoretical analysis of the directed graphs, generated by the partial order relation. For the programming language PYTHON,

see for example (Weigend 2006) or (Lutz and Ascher 2003). This program package comprises several features, e.g. main partial order analysis, fuzzy partial order, similarity analysis (Voigt et al. 2008a, b), dominance degree or sensitivity analysis.

In the current data analysis, the test sets of 11 Alpine monitoring sites times 17 pesticides concentrations in humus soil samples were examined with the newly developed feature of dominance degree analysis. This approach is also called DDS–domination–domination–separability. It was applied in order to detect a relationship between the concentrations of chemicals with the altitude of the monitoring performed.

In the stepwise DDS approach, it could be demonstrated that only among the altitude classes 4, 3, 1 and 0 a relationship exists. To complement the results, the main partial order analysis (Hasse diagram technique) was applied to the stepwise attribute reduction procedure. The most polluted regions were HD04 (1,450 m) and HD05 (1,650 m), which are those locations found in the highest located monitoring sites. The least polluted regions (in most steps) were those at approximately 800 m (HD01, HD07).

The altitude class 2, this means the altitude range at approximately 1,200 m a.s.l., is different from the other sites in all approaches, which may be of specific significance. The local characteristics of the two vertical profiles, such as different ecological parameters, may be possible factors influencing the results in the intermediate zone of 1,200 m a.s.l. The selection of sites along the Walchensee-Eschenlohe profile, which consists of two partial profiles at few kilometres horizontal distance between each other, may have an impact. Additionally, the existence of a so-called warm zone 400–500 m above valley ground experienced in Allgäu Alps (Frenzel and Fischer 1957) influences the vertical distribution of POP concentrations in soil. Temperature inversions are possible at the two sites of altitude class 2 which were selected on north-facing slopes. Such inversions are typically located above cool air reservoirs in the valleys (Whiteman 1982; Savov et al. 2002). Weaker winter insolation particularly at N-facing slopes enhances the probability of formation of a stable layer near the valley ground and a subsequent warmer slope zone some 100 m above it. Since we did not measure temperature at each site, all explanations are only presumptive.

It is foreseen that the particularities found along these altitude profiles will be investigated in a future campaign. It seems to be necessary to take samples from more sites in order to corroborate the significance of the results. Furthermore, other MONARPOP data from other Alpine countries, e.g. Austria, Switzerland, Italy and Slovenia, should be investigated using the Hasse diagram technique. There is a tendency that MONARPOP vertical profiles

from Central Alps show less irregularities at intermediate levels (1,200 m a.s.l.).

In conclusion, also the Hasse diagram technique reveals that the concentrations of the chemicals are not only generally different in higher alpine regions than in lower ones but also that they increase with altitude for most of the pesticides studied. Furthermore, the applied DDS method illustrated that a certain altitude in between the different profiles deviates from the continuous increase of pollution with altitude. Possible reasons are:

- deviations from a properly designed profile
- inversion and condensation layers, resp. irregularities of precipitation
- unidentified specific local contamination.

For small inorganic ions such as SO_4^{2-} , Miller and Friedland (1993) modelled and Sickles and Grimm (2003) could measure a deviation from a continuous increase or decrease of their deposition rates which was elaborated by the model caused by dry deposition and cloud water deposition along the forest canopy, which can serve as a most likely hypothesis to be specifically confirmed in future studies on organic pollutants in mountainous areas.

These results should be complemented in further studies with MONARPOP monitoring data from other Alpine countries, e.g. Austria, Switzerland, Italy and Slovenia.

Generally, caused by the numerous uncertainties identified in several campaigns, it is necessary to investigate the issue of organic pollutants in mountainous regions by means of carefully designed monitoring and modelling studies to encourage further investigations of the important processes in mountainous regions and to identify important parameters that control the occurrence and extent of cold condensation effects in mountain ranges.

Applying of mathematical simulation models is of high interest not only because of process analysis but also for validation. However, the problem is that running that kind of models needs certainly more geographical and climatic parameters in contrast to our ranking method which only needs the altitude as an environmental parameter. Further studies which cannot be in the frame of this paper will be initiated in the near future based on generic models like those, e.g. developed by Scheringer et al (2000, 2001) and Stocker et al (2007).

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