Mountain Cold-Trapping Increases Transfer of Persistent Organic Pollutants from Atmosphere to Cows' Milk

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Ⓢ Supporting Information

ABSTRACT: Concentrations of long-lived organic contaminants in snow, soil, lake water, and vegetation have been observed to increase with altitude along mountain slopes. Such enrichment, called "mountain cold-trapping", is attributed to a transition from the atmospheric gas phase to particles, rain droplets, snowflakes, and Earth's surface at the lower temperatures prevailing at higher elevations. Milk sampled repeatedly from cows that had grazed at three different altitudes in Switzerland during one summer was analyzed for a range of persistent organic pollutants. Mountain cold-trapping significantly increased air-to-milk transfer factors of most analytes. As a result, the milk of cows grazing at higher altitudes was more contaminated with substances that have regionally uniform air concentrations (hexachlorobenzene, α-hexachlorocyclohexane, endosulfan sulfate). For substances that have sources, and therefore higher air concentrations, at lower altitudes (polychlorinated biphenyls, γ-hexachlorocyclohexane), alpine milk has lower concentrations, but not as low as would be expected without mountain cold-trapping. Differences in the elevational gradients in soil concentrations and air-to-milk transfer factors highlight that cold-trapping of POPs in pastures is mostly due to increased gas-phase deposition as a result of lower temperatures causing higher uptake capacity of plant foliage, whereas cold-trapping in soils more strongly depends on wet and dry particle deposition. Climatic influences on air-to-milk transfer of POPs needs to be accounted for when using contamination of milk lipids to infer contamination of the atmosphere.

INTRODUCTION

Persistent organic pollutants (POPs) are resistant to degradation, have a high tendency for accumulation in organisms, and a relatively high environmental mobility.[1] Various health effects in humans and wildlife species have been linked to chronic exposure to low levels of POPs, and they are considered sufficiently hazardous to merit worldwide restrictions on their use and production.[1] The combination of persistence and mobility allows POPs to sometimes adopt environmental distribution patterns that are counterintuitive, in the sense that the highest concentrations are not always observed close to the point of release into the environment.[2] Thermodynamically and kinetically driven amplification processes[2,3] have been used to explain POP accumulation in regions remote from contamination sources,[4,5] which may be home to wildlife and human populations of unusually high susceptibility to the adverse effects of POPs.[6]

High elevations were identified as areas of potential POP amplification 25 years ago[7] through a process referred to as mountain cold-trapping. Concentration gradients in snow, soils, foliage, and fish that increase with altitude[8−14] have provided experimental evidence. The preferential accumulation of some POPs in high altitude regions has been attributed to precipitation that becomes more intense and colder and thus more efficient in depositing contaminants with increasing elevation.[11,15] The lower temperatures prevailing at higher altitudes relative to surrounding lower areas also slow down degradation and volatilization processes of POPs, further favoring their accumulation.

Grazing cows take up POPs deposited from the atmosphere to their pastures.[16] Because of their hydrophobic character, POPs that are resistant to metabolic transformation concentrate in milk fat.[16] Dairy products are therefore important vectors of human exposure to POPs, in particular for populations with a low intake of meat and fish from POP-contaminated waters.[6] The high rate of fat loss through lactation means that dairy
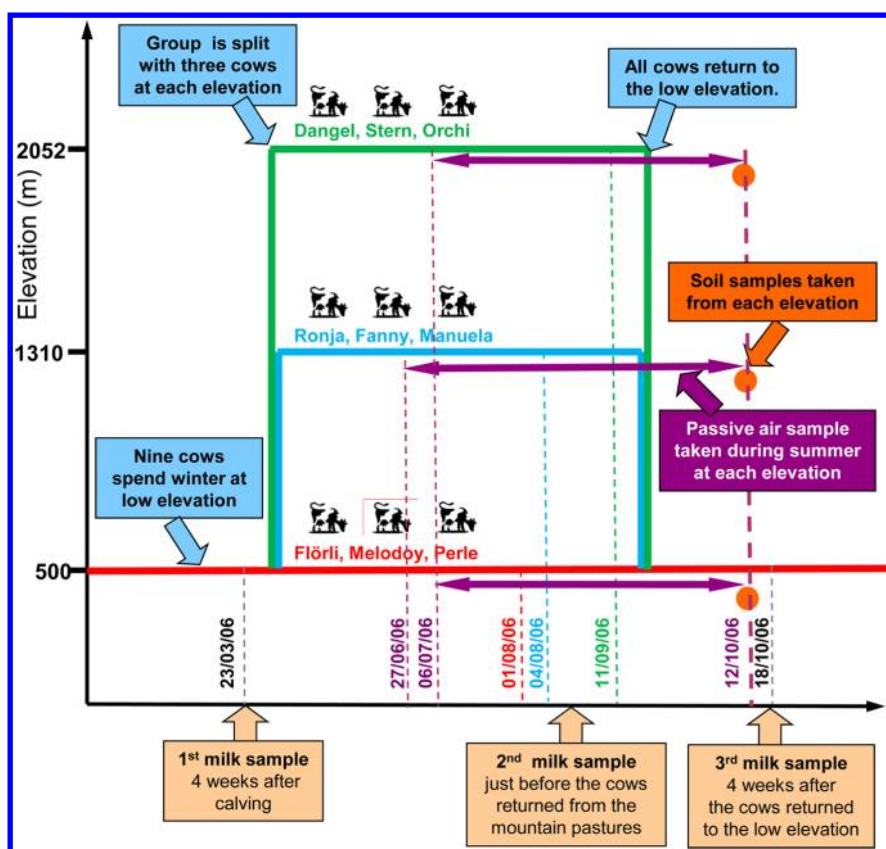
Figure 1. Schematic illustration of the experimental sampling design. A group of milk cattle that overwintered in the vicinity of Zürich (ca. 500 m above sea level) was split in spring 2006 to spend the summer at various pastures throughout Switzerland (Figure S1, Supporting Information). Milk from nine cows was collected three times: in March four weeks after calving, at the end of the summer that three cows each spent at pastures at either 500, 1310, 2052 m, and again in mid-October four weeks after they all returned to winter pasture at low elevation. Ambient contamination levels at the three summer pastures were characterized by measuring the long-term average POP concentrations in air between early July and mid-October and in soil samples taken in October.

cows quickly establish a steady state,[17] whereby the POP levels in milk reflect the contamination of the feed.[18]

While the presence of POPs in milk from cattle grazing on high alpine pastures has recently been confirmed,[19,20] no studies have looked at the potential impact of mountain cold trapping on contaminant levels in the milk of cows grazing at high altitude.[21] Here, we examine the time course of the levels of POPs in milk from cows that spent a summer grazing at three different altitudes in the Swiss Alps. The objectives were to address the following questions: Do POP levels in the milk of cows grazing at different altitudes provide further evidence for the process of mountain cold-trapping, and do they shed light on the mechanisms responsible for it? And further, if mountain cold trapping does occur, is the resulting increase in POP exposure relevant?

METHODS

Sampling. The study design is illustrated in Figure 1. Milk samples were collected from three groups of three cows that grazed at three different altitudes (500, 1310, and 2052 m) in the Swiss Alps (Figure S1, Supporting Information) during the summer of 2006 at three time points: (i) in mid-March, four weeks after calving when all cows were at a 500 m altitude and prior to the group being split to summer pastures at different altitudes, (ii) in August/September just before the cows returned from the mountain pastures at the end of summer, and (iii) in mid-October, approximately four weeks after the

cows returned to the low altitude farm, where they spend the winter. Sampling dates are given in Figure 1 and also in Tables S1, S3 and S4 of the Supporting Information. Milk was sampled from aluminum collection cans into 500 mL Nalgene bottles that had been pre-cleaned with hexane and air dried. The milk was stored frozen at −18 °C for between 4 and 32 weeks before being freeze dried in an industrial-scale freeze dryer at the Laboratory of Food Process Engineering at ETH Zürich and transferred to plastic bags. Except for PBDEs, no sample contamination during freeze drying was evident in vegetable oil that was subjected to the freeze-drying process alongside the milk samples and analyzed for the same analytes reported here.

Concentrations of the POPs in the atmospheric gas phase, averaged over the summer grazing season, were recorded through the use of XAD-based passive air samplers[22] deployed in duplicate at each of three elevations from July to October, 2006. The samplers consist of a stainless steel mesh cylinder filled with 20 g XAD-2 resin and suspended in a stainless steel shelter with an open bottom.[22] The samplers were prepared as described previously.[22] Upon retrieval, the mesh cylinders were sealed in aluminum tubes and stored in a freezer.

Soils were sampled in October 2006 in the vicinity of the air sampling sites at the three different altitudes. Each soil sampling site was divided into a grid and six to nine samples were collected with an auger, reaching a depth of 5 cm. The soils were then mixed with a clean steel shovel and bucket.[11] For each site, two subsamples were collected, wrapped in aluminum

foil that had been baked at 450 °C, and stored in a freezer. Soil water content was determined as described in Daly et al.[11] and ranged from 13% to 38%; the carbon contents of dried (50 °C, 3 h) and ground soils were determined with a Perkin-Elmer CHNS/O Analyzer 2400. Pasture grass was not sampled because very high spatial and temporal contamination variability makes it difficult to obtain representative samples[19].

Freeze-dried milk, soil, and air sampling resin were shipped to Canada for extraction and analysis.

Extraction, Clean-Up, and Quantification. Samples (20 g of XAD-resin, 15 g of wet soil, 3−4 g of freeze-dried milk) were mixed with baked sodium sulfate (soil, milk), spiked with isotopically labeled internal standards, and Soxhlet extracted overnight with either dichloromethane (air, soil) or a mixture of dichloromethane and hexane (50:50; V:V) (milk). Extracts were cleaned, reduced in volume, and spiked with additional labeled performance standards. Field and laboratory blanks were subjected to the same procedures as the actual samples. The extracts were analyzed for 56 PCB congeners, 21 pesticides, and 13 PBDE congeners using gas chromatography−mass spectrometry. Target analytes were selected to include bioaccumulative substances with a wide range of gas−particle partitioning and wet scavenging behavior. Details of the analytical procedure are provided in the Supporting Information.

Statistics. To investigate how concentrations of the chemicals in milk and soil and the air-to-milk transfer factors vary with time and location, analysis of variance with Turkey's post hoc multiple comparisons (IBM SPSS Statistics v20) were applied at a significant level of $\alpha = 0.05$ to the natural logarithm transformed concentrations.

■ RESULTS

Levels of POPs in Air, Soil and Cows' Milk. Several POPs were detected in air (Tables S1 and S2, Supporting Information), soil (Table S3, Supporting Information), and milk fat samples (Table S4, Supporting Information). These include hexachlorobenzene (HCB), α- and γ-hexachlorocyclohexane (HCH), components of chlordane (trans- and cis-chlordane, trans-nonachlor), and polychlorinated biphenyls (PCBs). Whereas α- and β-endosulfan and the degradation product endosulfan sulfate (EndoSO$_4$) were present in air, only EndoSO$_4$ was detected in soil and milk. We also found polybrominated diphenyl ethers (PBDEs) and traces of current-use pesticides in the soil and air extracts, including chlorothalonil, dacthal, pendimethalin, and trifluralin. Because the analysis of PBDEs in milk was compromised by sample contamination, only their levels in air and soil are presented in Table S5 and Figure S2 of the Supporting Information. Data for pesticides that were not detected in milk fat are also presented in Tables S1−S3 of the Supporting Information. In all three types of samples, HCB and PCBs were the dominant POPs (Figure S3, Supporting Information). The composition of the PCBs was similar in all samples of air, soil, and milk but varied widely between them (Figure S4, Supporting Information). The lighter PCB congeners, 15 and 52, were prevalent in air, whereas heavier congeners were dominant in soils. Only five PCB congeners were consistently detected in milk (99, 138, 153, 180, and 183).

A comparison of the concentrations of POPs measured here with those reported previously is included in Figures S5 and S6 and Tables S6 and S7 of the Supporting Information. It shows that Swiss alpine milk fat has concentrations of pesticides and

PCBs within the middle of the range recorded for central Europe. The levels of all measured POPs reported here are well below the maximum residue limit values (Table S8, Supporting Information) and their presence in the milk constitutes no health concern.

Figure 2 shows the concentration gradients with elevation for the six compounds or compound classes that were detected in all air, soil, and milk samples.

Concentration Gradients of POPs in Air. Concentrations of α-HCH, endosulfan-related compounds, and HCB in air were low and nearly uniform at the three locations (Table S2, Supporting Information, and Figure 2). Because POP concentration gradients in air tend to reflect proximity to ongoing sources, the absence of such gradients indicates very limited sources of those compounds along the transect, which is consistent with no current use in Switzerland, in some cases for many decades. Those POPs likely arrived in Switzerland by atmospheric transport from elsewhere. Concentrations of other compounds in air, namely, PCBs, chlordane-related substances, and γ-HCH declined with elevation (Figure 2), indicating that the lower pastures were closer to sources. The gradient is particularly pronounced for trans-chlordane (low pasture/high pasture (L/H) ratio >10), intermediate for γ-HCH and cis-chlordane (L/H ratio around 3 to 4), and smaller for PCBs and trans-nonachlor (L/H ~2.5). The lower pastures are close to the city of Zürich (~20 km), which is known to be an important current source of PCBs to the atmosphere despite the restricted status of PCBs in Switzerland.[23] The elevated levels of some pesticides at lower elevation suggest some recent use or continued emissions from use in the past (γ-HCH (lindane), chlordane).

Concentration Gradients of POPs in Soils. Concentration gradients of different POPs in soil varied widely, ranging from sharply increasing with elevation (EndoSO$_4$) to clearly decreasing with elevation (PCBs, HCB) (Table S3, Supporting Information, and Figure 2). The significance of any differences in soil concentrations is given in Table S9 of the Supporting Information. Whereas EndoSO$_4$ concentrations in air are uniform across the three elevations, concentrations in soil very clearly and significantly increase with increasing elevation, consistent with a high predicted[15] and previously observed[11] mountain cold-trapping potential for this substance that is due to the marked shift in how efficiently endosulfan-related substances are scavenged by precipitation within the temperature range encountered along elevation gradients.[15]

Although PCBs have previously been observed to undergo mountain cold-trapping,[12] accumulation at higher altitudes is not apparent in the current soil data. The gradient of significantly declining soil concentrations of $\sum$PCBs with elevation in the Swiss Alps is even more pronounced (low pasture/high pasture ratio ~5) than what was observed in air. However, this is partly due to the much larger number of congeners detected in the low elevation soils; the L/H ratio for the five congeners detected in all soils is only ~3 and thus close to the ratio in air. Ongoing emission of PCBs close to the lower end of the transect[23] likely masks any mild cold trapping that might be expected for the PCBs.[15]

Concentrations of HCB in soil also decline with increasing elevation but likely for different reasons as the amounts of HCB sequestered in the passive air samplers do not suggest that Zürich or other low-elevation areas in northern Switzerland are significant current sources of HCB. HCB is too volatile to be subject to wet atmospheric deposition processes. The air and
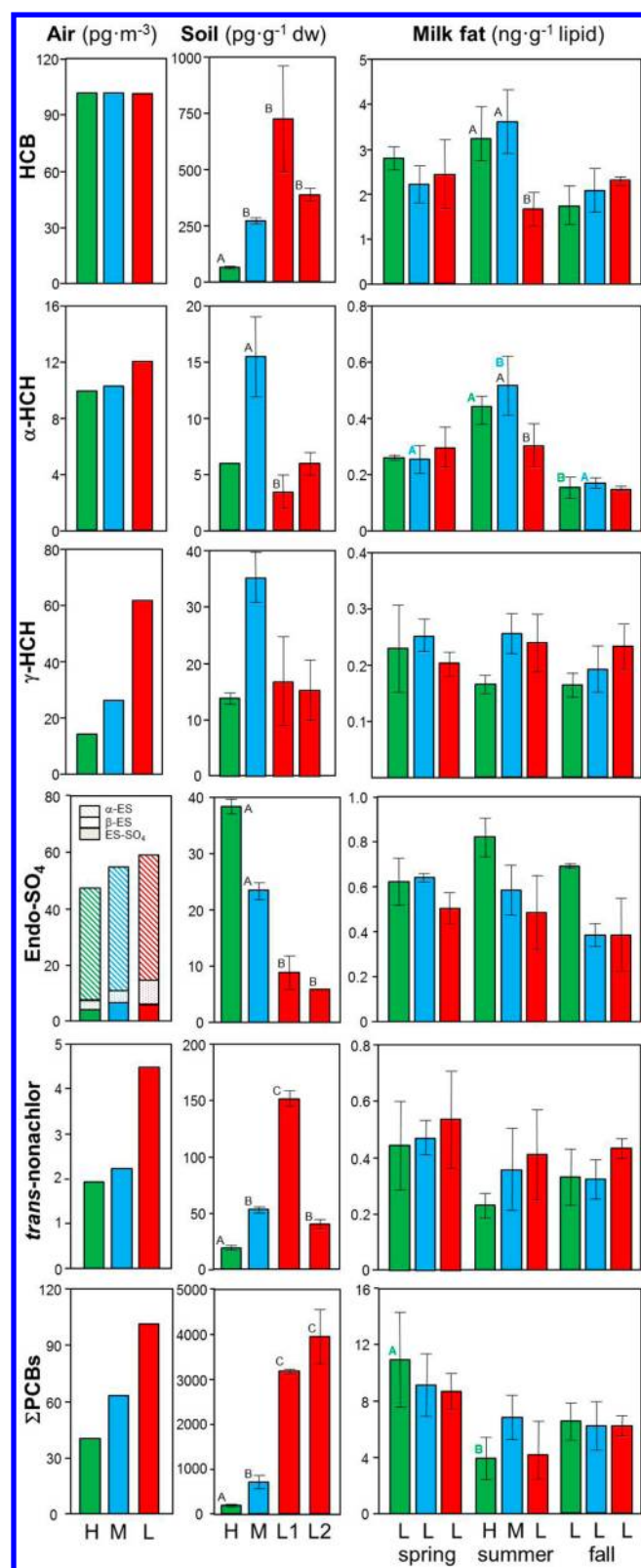
Figure 2. Concentration of hexachlorobenzene (HCB), α- and γ-hexachlorocyclohexane (HCH), endosulfan-related compounds (ES, endosulfan; EndoSO$_4$, endosulfan sulfate), *trans*-nonachlor, and polychlorinated biphenyls ($\sum$PCBs) in air, soil, and milk fat at high (green, H; Leisalp), middle (blue, M; Hinterschlattalp), and low (red, L) pastures. Concentrations in soil are given for two low elevation pastures (L1, Seegräben; L2, Hombrechtikon); air concentrations at these two pastures were the same. In the spring and fall, all cows were at the lower pastures; only in summer were the three groups of cows

Figure 2. continued

grazing at different altitude. The whiskers indicate either the two concentrations in duplicate samples (soils) or the standard deviation of the three concentrations in triplicate samples (milk); the air concentrations have no whiskers because the discrepancy between duplicates was uniformly very small. Where two bars have different black letters, the two concentrations from different elevations are statistically different from each other at the 95% confidence level. Where two bars have different letters of the same color, the two concentrations from different times are statistically different from each other at the 95% confidence level (Table S9, Supporting Information).

soil concentration gradients observed for HCB are consistent with the prediction of no cold-trapping behavior for a chemical that is not subject to precipitation scavenging.[15]

Both hexachlorohexanes had higher concentrations in soils from the middle pasture. Levels in soil from the high and low pasture are similar and in the case of α-HCH very close to the detection limit. This peak in soil concentrations at midaltitude does not match with the air concentration gradient of either HCH. This may suggest that some HCH-containing pesticide was used at or close to this midaltitude pasture in the past.

**Time Course of POPs Concentrations in Cows' Milk.** The concentrations of POPs in the milk sampled in March are not statistically significantly different between the three groups of cows (significance for all comparisons discussed here is given in Table S9, Supporting Information), confirming that they had very similar levels at the beginning of the study before the group was split at the beginning of summer. However, the change in concentrations in milk at the end of summer was very different for different POPs (Table S4, Supporting Information, and Figure 2). Levels of γ-HCH did not change significantly at any altitude, and PCB and *trans*-nonachlor levels dropped at all altitudes but only significantly so for PCBs at the highest pasture. Levels of α-HCH and HCB increased in the milk from cows that spent the summer at the two highest pastures (that increase is significant for α-HCH at Hinterschlattalp), and endosulfan sulfate levels increased in cows grazing at Leisalp but remained unchanged at the other two altitudes. Remarkably, concentrations in milk sampled in October is again very similar between the three groups of cows, suggesting that any differences that had developed during the summer were quickly lost after four weeks of feeding together at the low-elevation pasture. Only the group of cows spending the summer at the highest alp retained somewhat elevated levels of endosulfan sulfate into the fall. Generally, levels in October were either similar (TN, γ-HCH, HCB) or slightly lower than in spring (PCBs, α-HCH), but none of these changes were significant.

When comparing the concentrations in end-of-summer milk between the three groups of cows grazing at different altitudes, only HCB had significantly higher concentrations at the two higher pastures. Levels of α-HCH were significantly elevated at the middle alp compared to the low alp (Figure 2).

Concentrations of POPs in cows' milk have previously been shown to fluctuate seasonally,[18,19,24] which has largely been attributed to fluctuations of the contamination of the feed. For example, Tato et al.[19] observed that PCB concentrations in alpine milk followed the seasonal trend in the concentrations in vegetation. While there may be other factors that can influence temporal changes in milk contamination (such as mobilization of stored contaminants when fat is lost during the first few

month after calving[25]), the time trends and the end-of-summer differences in milk concentrations observed here are likely also caused by differences in feed concentrations. For example, the higher levels of α-HCH, HCB, and EndoSO$_4$ observed in the milk of cows grazing at higher altitude suggests that the high-elevation pastures had higher concentrations of these substances than those at Hombrechtikon and Seegräben during summer. Similarly, declining PCB concentrations during the summer observed in all cows irrespective of grazing altitude indicates that the meadows were less contaminated with PCBs than the feed during the winter. Tato et al.[19] had also observed a decrease in PCBs levels in alpine milk during the summer grazing season.

Air−Milk Transfer Factors. By dividing the concentration in milk at the end of summer in units of ng g^{-1} lipid by the concentration in air during summer in ng m^{-3}, air−milk transfer factors TF$_{A:M}$ in units of m^3 g^{-1} lipid[26] can be calculated for all three elevations (Figure 3). TF$_{A:M}$ vary by
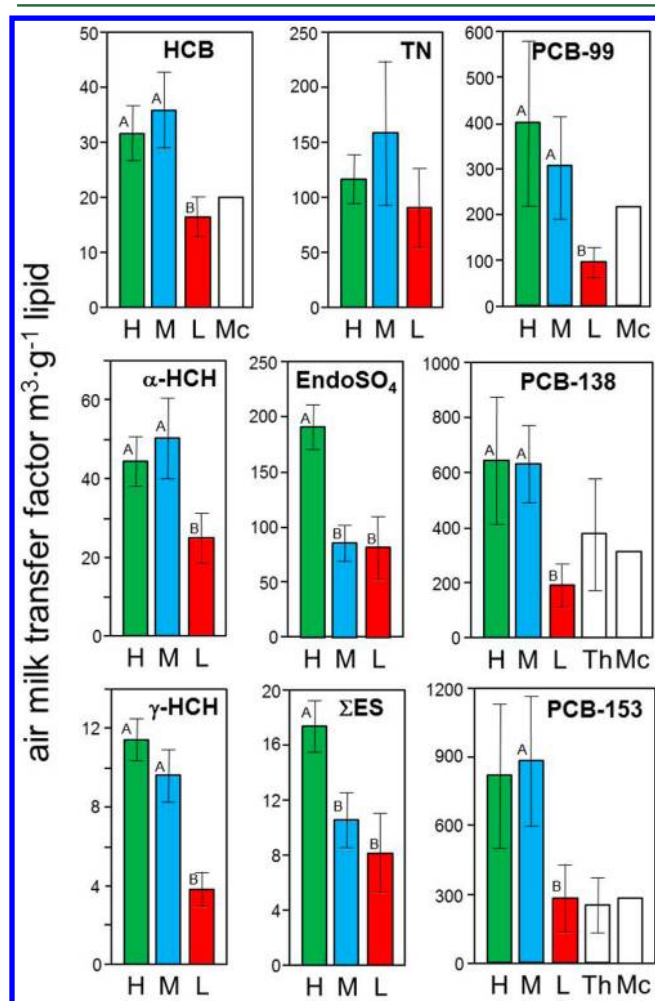
Figure 3. Air−milk transfer factors for selected POPs at the high (green, H), middle (blue, M) and low (red, L) elevation pastures during summer 2006. Also shown are transfer factors reported for HCB, PCB-99, PCB-138, and PCB-153 by McLachlan[16] (white, Mc) and Thomas et al.[26] (white, Th). The whiskers indicate standard deviation due to the variability in milk fat concentrations; the uncertainty in air concentration is not considered. Where two bars have different letters A and B, values are statistically different from each other at the 95% confidence level (Table S9, Supporting Information).

orders of magnitude between chemicals, the general trend being PCBs > TN > α-HCH ≈ HCB > $\sum$endosulfan > γ-HCH. Such differences are expected as the compounds differ widely in terms of deposition rate from air to pasture, efficiencies of uptake in the cow and transfer to the milk, and degradation loss in foliage, cows' gut, and organs. The TF$_{A:M}$ for HCB and PCB congeners 99, 138, and 153 at the lower elevation are in good agreement with those reported by McLachlan[16] and Thomas et al.[26]

The air−milk transfer factors give a much clearer picture than the somewhat inconsistent relationship between grazing altitude and concentrations in milk (Figure 2). The TF$_{A:M}$ were generally higher at the two alps in the mountains. For HCB, the two HCHs and the three PCB congeners, the TF$_{A:M}$ at the two higher elevation pastures was significantly higher than at the lower elevation; differences between the high and mid-elevation pasture are not significant. While TN also has higher TF$_{A:M}$ at the two higher elevation pastures, the differences are not significant. The TF$_{A:M}$ for EndoSO$_4$ is only significantly elevated at the highest pasture; this is the case whether the air concentration of endosulfan sulfate only or of all endosulfan-related substances is used in the calculation.

In principle, air-to-milk transfer between the groups of cows may differ because of differences in air-to-pasture transfer and/or feed-to-milk transfer during summer. Because no pasture grass was sampled, we cannot empirically attribute the observed differences in TF$_{A:M}$ to either process. In cows grazing at alpine sites in Switzerland, reduced milk yield compared to cow grazing at lower elevations has been observed and was partly attributed to reduced food intake related to hypoxia.[27] We also observed a trend toward lower milk yield and higher fat content at higher elevation (Table S10, Supporting Information). However, milk fat production at the higher pastures was only reduced by less than 25%, and the reduction was not significant (Table S10, Supporting Information). While the effect of reduced milk fat production at higher altitude may therefore have contributed to the observed trends in air-to-milk transfer factors with elevation, it is clearly insufficient to explain them. As such, it is unlikely that the differences in TF$_{A:M}$ are largely due to differences in food intake, energy expenditure, or lipid dynamics. We therefore attribute the differences in TF$_{A:M}$ for a compound mostly to differences in air-to-pasture transfer and possibly in degradation loss in the pasture. In other words, the higher TF$_{A:M}$ at the higher elevation pastures are indicative of higher air-to-pasture transfer and/or lower degradation loss, i.e., they are due to the very processes that are implicated in mountain cold-trapping of POPs.

Transfer to grass of relatively involatile POPs (with octanol−air equilibrium partition coefficients log K_{OA} exceeding 9.5) was found to be dominated by gaseous deposition.[28] If that is the case for relatively involatile POPs, gaseous deposition will be even more dominant in transferring the more volatile POPs discussed here (7.2 < log K_{OA} < 9.5)[29−31] into pasture grass. For relatively volatile POPs (log K_{OA} < 8) that reach equilibrium between air and foliage, the transfer from air to grass is strongly influenced by temperature because their uptake is governed by the temperature dependent uptake capacity of the grass.[32] A 10 K drop in temperature is estimated to increase transfer by more than a factor of 3.[32] Even for compounds with a log K_{OA} between 8 and 9, temperature is predicted to exert a notable influence on air to pasture transfer (see Figure 4 in ref 32). With the exception of PCB-138 and -153, all of the compounds with elevated TF$_{A:M}$ in Figure 3 have a log K_{OA}

below 9 and are thus expected to have considerably higher air-to-pasture transfer at higher elevation than at lower elevation. Even for less volatile POPs, for which uptake in the pasture is kinetically rather than thermodynamically controlled, it is conceivable that higher wind speeds and lower growth rates of grass lead to higher air-to-pasture transfer at higher altitude. Notably, higher PCB concentrations were recorded in a north-facing alpine pasture compared to a nearby pasture with southern exposure, which was attributed to higher temperatures of leafs receiving higher amounts of short wave radiation.[19]

Welsch-Pausch and McLachlan[28] noted marked differences in the importance of different atmospheric deposition pathways of relatively involatile POPs to soil and crops. While gaseous deposition dominated for crops, deposition to soil occurred largely by particle-bound deposition. Furthermore, soil contamination with POPs is a function of atmospheric deposition over many years, if not decades, whereas crop concentrations will largely reflect atmospheric conditions during the one season of its growth. As such, the measured POP concentration gradients in soil (Figure 2) cannot be assumed to reflect the POP concentration gradient in pasture grass, especially for the less volatile substances. We therefore refrained from using the measured soil concentrations to infer differences in air to pasture transfer at the three elevations. Also, while soil ingestion could be a major POP intake route for milk cattle in regions with highly contaminated soil,[24] it is not likely to be an important pathway in remote areas.[19]

DISCUSSION

The contamination of Swiss alpine cow milk with POPs, while generally low, is not as low as one might expect based on the remoteness of high-elevation summer pastures from sources of POPs. This is because mountain cold-trapping, i.e., the enhanced net atmospheric deposition to pastures at the lower temperatures prevailing at higher altitude, significantly elevates air-to-milk transfer. The observed increase in air-to-milk transfer between low and high elevation pastures in Switzerland was more than 3-fold for PCBs, approximately 2.5-fold for γ-HCH (lindane), and around 2-fold for HCB, α-HCH, and endosulfan-related substances. This implies that milk from cows grazing at high elevation can be significantly more contaminated with substances that have relatively uniform concentrations in air within Switzerland (i.e., HCB, α-HCH, endosulfan) compared to milk from cows grazing at low altitude. For substances that have sources and thus higher concentrations in air at low elevation (e.g., PCBs, γ-HCH, trans-nonachlor), mountain cold-trapping essentially counteracts the dilution of the contaminants with distance from source, resulting in milk contaminations that are not significantly dependent on summer grazing altitude.

Interestingly, this study suggest that the mechanism of cold trapping responsible for higher air-to-milk transfer is different from that observed in soil and water (and thus also fish) for which wet and particle-bound deposition is important. Because POP uptake in pastures occurs mostly by gaseous deposition,[28] cold trapping is due to the higher uptake capacity of foliage for relatively volatile POPs at lower temperatures. Wania and Westgate[15] had already suggested that "if dry gaseous deposition is the dominant deposition process, higher concentrations in foliage sampled at higher elevation can be caused by an increase in the foliage/air partitioning coefficient at lower temperatures". The temperature dependence of precipitation scavenging that underlies many other mountain cold-trapping phenomena[15] is less important in the context of grazing cattle because wet deposition contributes relatively little to the contamination of pasture grass. This also explains why air−milk transfer was elevated at high altitude (Figure 3) even though we did not observe cold trapping of PCBs, HCB, and chlordanes in Swiss mountain soils (Figure 2).

This is the first study to show that air-to-milk transfer of POPs is significantly influenced by climatic conditions. This source of variability needs to be accounted for when trying to use milk fat contamination to infer atmospheric concentrations of POPs.[26,33] For example, it is likely that using concentrations in Tibetan butter in combination with $TF_{A:M}$ for English cattle[26] to infer PCB concentrations in Tibetan air[34] leads to an overestimation of these concentrations.

ASSOCIATED CONTENT

Ⓢ Supporting Information
More detailed descriptions of methods and results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

REFERENCES

(1) Stockholm Convention on Persistent Organic Pollutants. http://chm.pops.int/Convention/ConventionText/tabid/2232/Default.aspx.
(2) Wania, F. On the origin of elevated levels of persistent chemicals in the environment. *Environ. Sci. Pollut. Res.* **1999**, *6*, 11−19.
(3) Macdonald, R.; Mackay, D.; Hickie, B. Contaminant amplification in the environment. *Environ. Sci. Technol.* **2002**, *36*, 456A−462A.
(4) Wania, F.; Mackay, D. Global fractionation and cold condensation of low volatility organochlorine compounds in polar regions. *Ambio* **1993**, *22*, 10−18.
(5) Scheringer, M.; Wegmann, F.; Fenner, K.; Hungerbühler, K. Investigation of the cold condensation of persistent organic pollutants with a global multimedia fate model. *Environ. Sci. Technol.* **2000**, *34*, 1842−1850.
(6) Undeman, E.; Brown, T. N.; Wania, F.; McLachlan, M. S. The susceptibility of human populations to environmental exposure to organic contaminants. *Environ. Sci. Technol.* **2010**, *44*, 6249−6255.

(7) Calamari, D.; Bacci, E.; Focardi, S.; Gaggi, C.; Morosini, M.; Vighi, M. Role of plant biomass in the global environmental partitioning of chlorinated hydrocarbons. *Environ. Sci. Technol.* **1991**, *25*, 1489−1495.

(8) Blais, J. M.; Schindler, D. W.; Muir, D. C. G.; Kimpe, L. E.; Donald, D. B.; Rosenberg, B. Accumulation of persistent organochlorine compounds in mountains of western Canada. *Nature* **1998**, *395*, 585−588.

(9) Grimalt, J. O.; Fernandez, P.; Berdie, L.; Vilanova, R. M.; Catalan, J.; Psenner, R.; Hofer, R.; Appleby, P. G.; Rosseland, B. O.; Lien, L.; Massabuau, J. C.; Battarbee, R. W. Selective trapping of organochlorine compounds in mountain lakes of temperate areas. *Environ. Sci. Technol.* **2001**, *35*, 2690−2697.

(10) Davidson, D. A.; Wilkinson, A. C.; Bais, J. M.; Kimpe, L. E.; McDonald, K. M.; Schindler, D. W. Orographic cold-trapping of persistent organic pollutants by vegetation in mountains of Western Canada. *Environ. Sci. Technol.* **2003**, *37*, 209−215.

(11) Daly, G. L.; Lei, Y. D.; Teixeira, C.; Muir, D. C. G.; Castillo, L. E.; Wania, F. Accumulation of current-use pesticides in neotropical montane forests. *Environ. Sci. Technol.* **2007**, *41*, 1118−1123.

(12) Chen, D.; Liu, W.; Liu, X.; Westgate, J. N.; Wania, F. Cold-trapping of persistent organic pollutants in mountain soils of Western Sichuan, China. *Environ. Sci. Technol.* **2008**, *42*, 9086−9091.

(13) Mast, M. A.; Alvarez, D. A.; Zaugg, S. D. Deposition and accumulation of airborne organic contaminants in Yosemite National Park, California. *Environ. Toxicol. Chem.* **2012**, *31*, 524−33.

(14) Arellano, L.; Fernández, P.; Tatosova, J.; Stuchlik, E.; Grimalt, J. O. Long-range transported atmospheric pollutants in snowpacks accumulated at different altitudes in the Tatra mountains (Slovakia). *Environ. Sci. Technol.* **2011**, *45*, 9268−9275.

(15) Wania, F.; Westgate, J. N. On the mechanism of mountain cold-trapping of organic chemicals. *Environ. Sci. Technol.* **2008**, *42*, 9092−9098.

(16) McLachlan, M. S. Bioaccumulation of hydrophobic chemicals in agricultural food chains. *Environ. Sci. Technol.* **1996**, *30*, 252−259.

(17) McLachlan, M. S. A simple model to predict accumulation of PCDD/Fs in an agricultural food chain. *Chemosphere* **1997**, *34*, 1263−1276.

(18) Lake, I. R.; Foxall, C. D.; Fernandes, A.; Lewis, M.; Rose, M.; White, O.; Dowding, A. Seasonal variations in the levels of PCDD/Fs, PCBs and PBDEs in cows' milk. *Chemosphere* **2013**, *90*, 72−79.

(19) Tato, L.; Tremolada, P.; Ballabio, C.; Guazzoni, N.; Parolini, M.; Caccianiga, M.; Binelli, A. Seasonal and spatial variability of polychlorinated biphenyls (PCBs) in vegetation and cow milk from a high altitude pasture in the Italian Alps. *Environ. Pollut.* **2011**, *159*, 2656−2664.

(20) Parolini, M.; Guazzoni, N.; Binelli, A.; Tremolada, P. Polybrominated diphenyl ether contamination in soil, vegetation, and cow milk from a high-mountain pasture in the Italian Alps. *Arch. Environ. Contam. Toxicol.* **2012**, *63*, 29−44.

(21) Daly, G. L.; Wania, F. Organic contaminants in mountains. *Environ. Sci. Technol.* **2005**, *39*, 385−398.

(22) Wania, F.; Shen, L.; Lei, Y. D.; Teixeira, C.; Muir, D. C. G. Development and calibration of a resin-based passive sampling system for persistent organic pollutants in the atmosphere. *Environ. Sci. Technol.* **2003**, *37*, 1352−1359.

(23) Gasic, B.; Moeckel, C.; MacLeod, M.; Brunner, J.; Scheringer, M.; Jones, K. C.; Hungerbühler, K. Measuring and modeling short-term variability of PCBs in air and characterization of urban source strength in Zürich, Switzerland. *Environ. Sci. Technol.* **2009**, *43*, 769−776.

(24) Mamontova, E. A.; Tarasova, E. N.; Mamontov, A. A.; Kuzmin, M. I.; McLachlan, M. S.; Khomutova, M.Iu. The influence of soil contamination on the concentrations of PCBs in milk in Siberia. *Chemosphere* **2007**, *67*, S71−S78.

(25) Thomas, G. O.; Sweetman, A. J.; Jones, K. C. Input-output balance of polychlorinated biphenyls in a long-term study of lactating dairy cows. *Environ. Sci. Technol.* **1999**, *33*, 104−112.

(26) Thomas, G. O.; Sweetman, A. J.; Lohmann, R.; Jones, K. C. Derivation and field testing of air−milk and feed−milk transfer factors for PCBs. *Environ. Sci. Technol.* **1998**, *32*, 3522−3528.

(27) Leiber, F.; Kreuzer, M.; Leuenberger, H.; Wettstein, H.-R. Contribution of diet type and pasture conditions to the influence of high altitude grazing on intake, performance and composition and renneting properties of the milk of cows. *Anim. Res.* **2006**, *55*, 37−53.

(28) Welsch-Pausch, K.; McLachlan, M. S. Fate of airborne polychlorinated dibenzo-p-dioxins and dibenzofurans in an agricultural ecosystem. *Environ. Pollut.* **1998**, *102*, 129−137.

(29) Xiao, H.; Li, N.; Wania, F. A compilation, evaluation and selection of physical chemical property data for *α*, *β* and *γ*-hexachlorocyclohexane. *J. Chem. Eng. Data* **2004**, *49*, 173−185.

(30) Shen, L.; Wania, F. Compilation, evaluation and selection of physical-chemical properties for organochlorinated pesticides. *J. Chem. Eng. Data* **2005**, *50*, 742−768.

(31) Schenker, U.; MacLeod, M.; Scheringer, M.; Hungerbühler, K. Improving data quality for environmental fate models: A least-squares adjustment procedure for harmonizing physico-chemical properties of organic compounds. *Environ. Sci. Technol.* **2005**, *39*, 8434−8441.

(32) McLachlan, M. S.; Welsch-Pausch, K.; Tolls, J. Field validation of a model of the uptake of gaseous SOC in *Lolium multiflorum* (Welsh Ray Grass). *Environ. Sci. Technol.* **1995**, *29*, 1998−2004.

(33) Weiss, J.; Müller, A.; Vives, I.; Mariani, G.; Umlauf, G. Spatial gradients of OCPs in European butter—Integrating environmental and exposure information. *Environ. Sci. Pollut. Res.* **2013**, *20*, 2948−2962.

(34) Wang, Y. W.; Yang, R.; Wang, T.; Zhang, Q.; Li, Y.; Jiang, G. Assessment of polychlorinated biphenyls and polybrominated diphenyl ethers in Tibetan butter. *Chemosphere* **2010**, *78*, 772−777.