Final Report

California Department of Water Resources

Contract B-80933

In Situ Se Volatilization and Form Measurements at San Joaquin Valley Evaporation Basins

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January, 1999

EXECUTIVE SUMMARY

In recent years, we have established that laboratory cultures of algae isolated from Tulare Lake Drainage District (TLDD) evaporation basin waters are capable of volatilizing Se, while depleting Se from the culture medium. The chemical forms of volatlization were the organic selenium compounds dimethylselenide (DMSe), dimethylselenenylsulfide (DMSeS) and dimethyldiselenide (DMDSe), all likely to be a result of microphyte activity. Thus, Se bio-volatilization may be an important route that contributes to the "disappearance" of waterborne Se observed at TLDD basins in recent years. It can also be an important link to both ecotoxic risk and remediation, depending on the specific biogeochemical transformations.

To gain direct evidence for the volatilization of Se and of biogenic Se forms, on-site collection and measurement of volatile Se forms was conducted at TLDD Hacienda basins (a "low" Se site), the Lost Hills Water District (LHWD) evaporation basins (a "high" Se site), and the San Luis Drain (SLD) in Kesterson Wildlife Refuge (a non-evaporation basin agricultural drainage water). This document reports the findings from a DWR-supported collaborative effort between ourselves and Dr. David Amouroux of CNRS in France. It describes open-air collection and measurement of volatile Se forms, using ultra-trace analysis of on-site gas chromatography-atomic fluorescence spectrophotometry (GC-AFS) and (back in France) the laboratory GC-inductively coupled plasma mass spectrometry (GC-ICP/MS). The text discusses the rationale of the open-air collection approach - as compared with box enclosure and box-model (wind fetch) methods - in order to avoid altering the biogeochemistry, while achieving measurement of Se forms at trace concentrations, and to address the expected heterogeniety of the evaporation basins.

The three principal forms, DMSe, DMSeS, and DMDSe, were clearly present in most air samples. DMSe tended to dominate in all cases, accounting for 69-100% of the total volatile Se (TVSe). The corresponding water samples also yielded DMSe, DMSeS, and DMDSe, with DMSe dominating the %TVSe. A glaring exception to this was the TLDD basin A2 samples, in which DMSe was a minor part of the %TVSe. As this basin receives water from the same inlet as basin C2, the large difference in volatile Se profile between A2 and C2 implies that they have a significant difference in the biogeochemistry. This is interesting in light of our previous findings that there is much higher Se bio-volatilization potential in C2 than in A2.

The heterogeniety of the basins were also reflected in the results. The predominantly downwind sites at TLDD - the southeast quadrants of basins C2 and A2 - exhibited higher TVSe than upwind (northwest) sites. This trend was expected based on our earlier findings of higher Se levels in the downwind sediments, where the cyanobacterial mats and detrital material accumulate.

A potentially important advance was the joint development of a method that allows interfacing of the open-air sampling system to all gas analysis instruments. The device used was a solid-phase microextraction (SPME) fiber. Application of the SPME interface to GC/MS analysis directly led to the discovery that volatile alkylbenzene compounds has a strong correlation to DMSe production over all sites measured ($r^2 > 0.75$ for toluene). The correlation was particularly strong at TLDD ($r^2 > 0.98$ for toluene). These alkylbenzene compounds are probably a result of microphyte and microbial metabolism. Since the alkylbenzene compounds are: (a) the "BTEX" chemicals with inexpensive portable monitors available, and (b) are present at appropriate concentrations for such detection equipment, this finding opens the possibility for using BTEX as a surrogate measure of Se volatilization. If so, this can lead to the development of a rapidly-deployable, relatively low-cost, continuous monitoring, non-invasive volatile Se analysis system.

I. BACKGROUND

In recent years, we have established that laboratory cultures of algae isolated from Tulare Lake Drainage District (TLDD) evaporation basin waters volatilize Se, while depleting Se from the culture medium (Fan et al. 1997; Fan and Higashi, 1998; Fan et al., 1998). We have also demonstrated that dimethylselenide (DMSe) is the major volatile form, while dimethylselenenylsulfide (DMSeS) and dimethyldiselenide (DMDSe) are forms of volatile Se at lesser amounts (Fan et al. 1997; Fan and Higashi, 1998; Fan et al., 1998a). Laboratory mass balance studies indicate that these are the only significant forms of Se that

volatilize from the waters of TLDD. The fact that these organic selenides are the major forms of volatile Se indicates the workings of a biochemical mechanism(s) (Fan et al., 1998b). In any case, Se volatilization may be an important route that contributes to the "disappearance" of waterborne Se observed at TLDD basins in recent years. It can also be an important link to both ecotoxic risk and remediation, depending on the biogeochemical pathways that define the chemical forms of Se (Fan et al., 1998a).

To gain direct evidence for the volatilization of Se and of biogenic Se forms, on-site collection and measurement of Se forms volatilization was needed. Invasive methods, such as box enclosures, are traditionally used for high precision measurements of volatile compounds, but can alter the biogeochemistry rapidly. To be field-manageable, such boxes are also low volume (typically < 1 m^3), so that small changes in biogeochemistry can significantly affect the results. In addition, for Se the low volume limits analytical detection, so that analysis is usually confined to total Se even with long collection times (e.g. >> 1hr). The long collection times, in turn, increase the changes in biogeochemistry. Thus, although the approach has high chemical precision for measuring static sources at high concentration, it lacks both precision and accuracy in situations that have active biogeochemistry producing trace-level gases. Of course, Se biogeochemistry is just such a case, which is probably why volatilization studies are rare.

Conventional non-invasive methods, such as the box model (boundary layer/wind fetch) approaches, necessarily sample large areas and is therefore not useful given the small-scale (probably less than tens of meters level) heterogeniety of drainage basins; it also has heavy requirements of personnel and equipment, as we have experienced (Fan and Higashi, Salinity/Drainage rpt). As with the box enclosure approach, this approach is severely limited by the analytical methods to long durations while still lacking of Se form analysis. For the long term, the existing approaches are not likely to be developed into rapidly-deployable, relatively low-cost, and/or continuous monitoring, non-invasive Se analysis systems, all of which is required to address the high spatial and temporal variability of biogeochemically-active drainage waters.

This document reports the findings from a DWR-supported collaborative effort between ourselves and Dr. David Amouroux of CNRS in France. It describes on-site collection and measurement of volatile Se forms and the development of a straightforward method that allows interfacing to all gas analysis instruments with no instrument modifications. The latter directly led to a discovery that opens the possibility for the development of a rapidly-deployable, relatively low-cost, continuous monitoring, non-invasive volatile Se analysis system.

II. APPROACH & METHODS

Approach

The general approach to measure volatile Se forms was to use the near-liquid nitrogen temperature trap system developed by Drs. David Amouroux and Olivier Donard at CNRS/University of Pau in Pau, France. This system has been utilized by them on shipboard to trap volatile Se and determine their chemical forms over estuaries in Europe and in South America (Amouroux and Donnard, 1996). The near-liquid nitrogen temperature allows all volatilized Se to be trapped in their original forms which are then analyzed by a trace-analysis (pmole/l) gas chromatography-atomic fluorescence spectrophotometry (GC-AFS) on-site and ultra-trace analysis (fmole/l) GC-inductively coupled plasma mass spectrometry (GC-ICP/MS) back in France. The nature of the apparatus eliminates the common problem of trapping liquid oxygen which interferes with subsequent analysis and with trapping for longer durations. The analytical sensistivity allows short-duration (1 hr) sampling times, which makes measurement of multiple sites feasible.

In conjunction with air sampling, a water sample is purged with helium gas and the volatiles trapped in the same system as for air sampling. The quantity of Se forms in the air and water, together with the water temperture, pH, wind speed, salinity, and physical chemical properties (e.g. Henry's Law parameter) of each Se form, allows an calculation of the volatilization flux of each Se form from low-wind velocity saline waters (Andreae et al., 1994, modified from Liss and Merlivat, 1986, as applied by Amouroux and Donnard, 1996). The general form of the calculation is essentially Fick's law:

$$F = K \bullet C_w \qquad (1)$$

where F is flux density (nmoles/m^2 • hr), K is the transfer velocity (m/hr) that is a function of several parameters, and C_w is the concentration in water of the Se form of interest.

In equation (1), all the complexity is rolled into the K factor. Amouroux and Donnard (1996) had previously established a key step for K, which was to determine Henry's parameter for a Se form, such as DMSe, that was applicable outside of the laboratory, e.g. in saline waters. This was achieved by measurement of Se forms in air in conjuction with the water. As shown in Figure 1, they had also shown a strong relationship between chlorophyll *a* (a measure of microphyte population) and total volatile organic selenides (Amouroux and Donnard, 1996).

Therefore, the stage was set for some air and water measurements of Se forms. With support from DWR, we invited Dr. Amouroux and his assistant, Mr. Herve Pinaly, to bring their equipment over and conduct the prescribed Se measurements. Our contibution was to provide logistics and support for field studies plus conduct more detailed laboratory investigations, such as Se bio-volatilization potential studies (Fan et al. 1997; Fan et al., 1998a), supported by the UC-Salinity Drainage Program. As part of this DWR project, we also developed a procedural and instrument interface to their sampling system for GC-mass spectrometry (GC/MS), for broad-screen organic analysis and confirmation of Se form structures; this was a capability they had not tapped before. We had previously used the GC/MS for analysis of various Se organic forms, including volatile ones (Fan et al. 1997; Fan et al., 1998a).

Sampling Locations

The TLDD Hacienda basins represent a "low" Se site, the Lost Hills Water District (LHWD) evaporation basins represents a "high" Se site, and we included a section of the San Luis Drain (SLD) in Kesterson Wildlife Refuge for a non-evaporation basin agricultural drainage water. For the TLDD basins, we wanted to obtain measurements for at least two locations within a basin, as our earlier work had shown considerable heterogeniety due to wind-driven patterns of biota and detrital material (Fan and Higashi – Salin/Drain report)

Sampling Methods

The schematic and functioning of the Amouroux-Donnard air sampling apparatus is described in Figure 2, and is nearly identical to the system used previously (Amouroux and Donnard, 1996). Therefore, only a brief drscription is provided here. In the present study, we fixed 1/8 inch x 15 m Teflon air intake (Fig. 2) to the mast of a floating styrofoam board, which also housed the air temperature and wind velocity meters. The intake pipe also serve as the link to the remainder of the sampling appratus on-shore. Sampling was at 500ml/min for 1hr in all cases.

Corresponding water samples were collected by immersing a polypropylene bottle at the end of each air sampling, from the same location. They were stored on ice until purged as described in Fig. 2.

Note that (Fig. 2) trapped Sesamples are collected in glass U-tubes which can be stored in liq. nitrogen indefinitely; for all samplings, one sample was analyzed on-site by AFS, and duplicates were obtained either for GC/MS analysis or to transport back to France for ICP/MS analysis.

Analysis Methods

The analysis methods for AFS and ICP/MS are described elsewhere (Amouroux and Donnard, 1996), so only a brief description will be provided here. The schematic of the analysis is shown and described in Figure 2. The GC-AFS analysis is specific for Se compounds, and despite the portability, achieves detection limits of 0.1 pmole/l, which is sufficiently sensitive to quantify Se forms after just 1hr of sampling in estuaries low in Se concentration. The GC-ICP/MS analysis is multielement-specific; for example it can be set to monitor S and Se simultaneously. It can reach considerably lower detection limits than even the AFS detector, into the low fmole/l range, so it served as both a "safety net" for the project and to obtain information on non-Se volatile compounds.

On the other hand, the U-tube sample trap and system in Figure 2b is not compatible with conventional GC sample inlets, such as that of our GC/MS that is used for our volatile Se studies. Therefore, we set out to develop two possible means to interface the sampling system with GC/MS.

The first approach we tried was to desorb the U-tubes as in Figure 2, but to cryo-trap directly on the GC column using a GC-cryofocusing system (Scientific Instrument Services). This device maintains a one cm section of a GC column at liquid N_2 temperature, which takes the place of the second U-tube of Fig. 2b. While this approach basically worked, there were major problems with physical handling of the transfer line to the GC instrument, and the long time it took to transfer the sample to the GC column. The former is due primarily to the lack of custom hardware, but the latter is a limitation of the very small column volume (<0.01 ml) of high resolution GC instruments.

Therefore, we switched to a second approach, which was based on a new device we had used successfully in the past. The device is known as solid-phase microextraction (SPME) fiber (Pawlizyn refs), which is a one cm section of quartz fiber coated with an organic film (Figure 3a). The physical chemistry is engineered such that the coating achieves very high equilibrium at room temperature towards trapping volatile organic compounds, without degrading them. But at the high temperatures (280 °C) of a GC injector, the compounds are readily desorbed. To facilitate its use, the fiber is assembled into a syringe-like arrangement (Figure 3b) which simplifies introduction of the fiber through a septum into both a sealed sample chamber (e.g. the U-tube) as well as a standard GC injector. Thus, the SPME fiber device readily "interfaces" between the U-tube and our GC/MS, eliminating custom hardware configurations. Although expensive, each fiber is reusable for a few dozen times.

The details of the GC/MS analysis follows. For the volatile Se forms, we used a single SPME fiber coated with 25 µm thickness of carboxen/polydimethylsiloxane (PDMS) (Supelco Inc., Bellefonte, PA, USA), cleaned for >10 min at 280 °C under H_2 flow. It was inserted for 25 min into a Teflon-lined septum-capped sample U-tube heated to 50 °C, which ensured maximal transfer of volatile Se compounds from the U-tube surfaces to the SPME fiber. The fiber was then inserted into the GC/MS injector, which was at 280 °C and H_2 flow of approximately 0.3 ml/min. This procedure resulted in approximately 95% recovery of DMSe in a U-tube. For analysis of the next sample, the fiber was again thermally cleared and the process was repeated using the same fiber for all samples.

GC/MS analysis conditions were as follows: Varian 3400 GC (Varian Inc., Walnut Creek, CA, USA) with retention gap column of 0.53 mm x 1 mm 1.5µm coat DB5 phase (J&W Scientific, Rancho Cordova, CA, USA), the main column was 0.15mm x 50m 0.4um BPX-5 phase (SGE Inc., Austin, TX, USA), injector = 280 °C, column held at 40 °C for 2min, increased at 10 °C/min to 200 °C, H_2 carrier gas = 40 cm/s. The split valve was off for 2min, then on for the duration of the run. The GC was interfaced via a line-of-sight transfer line at 200 °C to a Finnegan ITD 806. Mass spectrometer conditions were as follows: manifold = 220 °C, electron energy = 70 eV, full scan acquisition m/z 55-200, 8 scans/sec averaged to give 1 scan/sec, automatic gain control = 54 amu, electron multiplier = 1250 V.

III. RESULTS AND DISCUSSION

Analyses of Se Forms by GC-AFS and GC-ICP/MS

Figure 4 shows an example chromatogram from on-site analysis of an air sample over an evaporation basin at TLDD. Although the conditions were adverse, the on-site analysis functioned with only minor problems, and was crucial to evaluating whether a sampling operation was successful.

Table I shows the results of air sample U-tube cryotrap analyses by GC-ICP/MS; the on-site GC-AFS gave comparable results.. The three principal forms of volatile Se, DMSe, DMSeS, and DMDSe are clearly present in many cases, as seen in our laboratory studies (Fan et al. 1997; Fan et al., 1998a). DMSe tended to dominate in all cases, accounting for 69-100% of the total volatile Se (TVSe). Note that repeated measurements at the same site, varying from minutes to 24 hr apart (for TLDD C2-SE and C1-SE, for

LHWD North Pond-S, and the two SLD samples) yielded different results. This variability was fully expected because these systems are very dynamic.

Table II shows the results of water purging analysis by GC-AFS. As with the air samples, the corresponding water samples yielded DMSe, DMSeS, and DMDSe, and the results again varied with repeated measurements. As with the air, DMSe dominated the %TVSe, but a glaring exception to this was the TLDD basin A2 samples, in which DMSe was a minor part of the %TVSe. Unfortunately, we lacked the time to collect the corresponding air samples in this basin. This difference is interesting because the TLDD basin series C and A are located near each other and share the same water inlet. The observed reverse profile between C2 and A2 implies a significant difference in the biogeochemistry between these basins, supporting our previous findings that there is much higher Se bio-volatilization potential in C2 than in A2 (Fan and Higashi, Salin/Drain rpt).

The two tables also show that concentrations of volatile organic Se forms are much lower at LHWD North Pond and SLD, than at TLDD. This is despite the nearly 100-fold higher total Se concentration of LHWD water, which was at that time approximately 860 ppm (see accompanying report). Again, this surprising result is probably due to differences in the biogeochemistry. Also note that LHWD South Pond water was over ten-fold higher in the volatile organic Se forms than the North Pond.

From Tables I and II, it can be seen that the predominantly downwind sites at TLDD - the southeast (SE) quadrant of basins C2 and A2 - exhibited higher TVSe than upwind (northwest, or NW) sites. This trend was expected based on the higher Se levels in the downwind sediments (Fan and Higashi, Salin/Drain Rpt), where the cyanobacterial mats and detrital material accumulate. This phenomenon is observed by even the casual visitor due to the very soft sediment and stench of sulfides and possibly selenides that is always highest at the downwind sites.

Flux of Se Forms

Table III shows the fluxes of DMSe calculated by Dr. Amouroux, based on the data in Tables I and II. The fluxes (last column) range more than two orders of magnitude among the sites that we measured in this one-week campaign. The calculated fluxes bear out all of the above discussions of site (location), temporal, and within-site spatial variability.

How much can Se form volatilization vary, and what are some of the forces of change? To get a feel for this, Figure 5 shows selected outputs of Dr. Amouroux's flux model for DMSe, anchored by the site-specific measurements in Tables I & II. The top two shows that the two quadrants of even a single basin can have different responses to wind speed and temperature. For comparison, the model output for LHWD North Pond is also shown, using a 10-fold lower scale for the flux. Clearly, there are differences between: (a) sites or locations; (b) seasons, as implied by the temperature axis; and (c) short time spans, due to changes in wind speed. All this is *imposed by only two environmental factors*. Of course, temperature and wind speed can be interactive with chemical reactions, microphyte/microbial community structures, and a number of other factors that could affect the DMSe production. There is also other Se forms to consider, as we saw in the comparison of C2 and A2 basins (Table II).

Interfacing a GC/MS: Confirmation of DMSe and Comparison with GC-AFS

For structural confirmation of volatile Se compounds, and in order to better observe the relationships between volatile Se forms and other compounds, there was a need to interface the cryotrap U-tube to a GC/MS. As described in Approach & Methods, the solution we developed was to turn to a newly-introduced carboxen/PDMS phase SPME fiber device. As shown in Fig. 3, the SPME fiber is physically configured like a syringe, which is first inserted into the sealed, heated sample U-tube through a septum to transfer the volatile compounds onto the fiber. Then the fiber is inserted into the conventional GC injector, which desorbs the compounds at high temperature.

Figure 6 top panel shows the total ion chromatogram (i.e. the entire data set) of an SPME-GC/MS analysis of C2-SE sample. There are about four dozen compounds of appreciable concentration in this

sample, as is seen from the large number of peaks. The middle panel of Figure 6 shows a "selected ion chromatogram", showing only compounds that have a ion mass (m/z) of 110 Daltons. This is selected to reveal and quantify DMSe (molecular weight of 110 Daltons on one of the isotopes) while rejecting most other compounds. DMDSe, DMSeS, DMS, and DMDS was also quantified in this manner, but using different ion masses. The whole mass spectra (not shown) confirms the identity of each peak.

Figure 7 shows an intercomparison of analysis by SPME-GC/MS and GC-AFS, by quantifying the DMSe peak on duplicate samples. The correspondence is good, considering variability between duplicate samples and the adverse field conditions under which the GC-AFS was run. In addition, the correlation value is conservative, since 3-5 ng was the detection limit of the SPME-GC/MS, which accounts for the flat response shown by the GC/MS below 450 pmol/l on the GC-AFS. At higher concentrations, e.g. the three data points to the right, the intermethod comparison appeared to be linear and very good ($r^2 > 0.95$).

Analysis of Cryotrap Contents by GC/MS

It is generally thought that DMSe shares the same biochemical pathway as its sulfur analog, DMS. If so, it would be expected that high DMS concentrations would correlate with high DMSe. A comparison of the DMS and DMSe water concentrations, as determined by SPME-GC/MS, is shown in Figure 8. The top panel plots **all** the samples subjected to SPME-GC/MS analyses, which includes water from TLDD, LHWD, SLD, and a laboratory experiment with TLDD water. Note that there are no data points in the upper right; that is, there are no cases where high DMS is accompanied by high DMSe, and vice versa.

Biogeochemically, DMDS may share only part of the pathways of DMS production. If we normalize DMS production to generation of DMDS, we might reveal whether DMS production is being inhibited by DMSe synthesis. The middle panel of Fig. 8 shows that normalized DMS appears to have the same negative, non-linear relation with DMSe as the top panel of Fig. 8. The bottom panel plots this on a log-log scale, and supports the presence of a negative relationship.

Are there relationships of DMSe production to other volatile compounds? We can readily address this, since the SPME-GC/MS method is not limited to S or Se compounds, and will detect unknown and unexpected volatile constituents. The bottom panel of Figure 6 illustrates a chromatogram based on a mass of 91 Daltons. This reveals alkyl-substituted aromatic compounds, such as toluene that is produced by many microorganisms. Figure 9 top panel plots all the samples subjected to SPME-GC/MS analyses, which includes water from TLDD, LHWD, SLD, and a laboratory experiment with TLDD water, with the exception of a single sample from LHWD. The latter was a considerable outlier, possibly due to analytical error. Note in Fig. 9 that there is a strong ($r^2 > 0.75$) relation of DMSe to toluene concentrations, which is striking considering the diverse environments represented by the samples. The bottom panel of Fig. 9 plots only the field samples from TLDD (all basins), and the relationship jumps to $r^2 > 0.98$! This strength of correlation is rarely seen in environmental chemistry. Other alkyl-benzenes (tentatively identified as ethylbenzene and dimethylbenzenes) also had correlations of $r^2 > 0.95$ for TLDD. Note that these are essentially the "BTEX" (benzene-toluene-ethylbenzene-xylene) chemicals monitored in factories.

If the BTEX-DMSe relationship holds up, it can represent a breakthrough in the analysis of volatile Se compounds. There are several reasons for this: (a) the toluene in Fig. 9 is estimated to be approximately million-fold higher concentration than DMSe, making its quantification far easier; (b) DMSe is very labile, while samples of toluene are generally much easier and convenient to trap and store, since it is very stable; (c) there are commercially-available, very practical personal (i.e. battery-powered, relatively low-cost, and easy maintenance) monitoring equipment for BTEX. Using BTEX as a surrogate for DMSe analysis opens up the possibility of near-real-time volatile Se monitoring at multiple locations over water bodies, for a low cost per sample not possible to achieve with direct Se analysis methods.

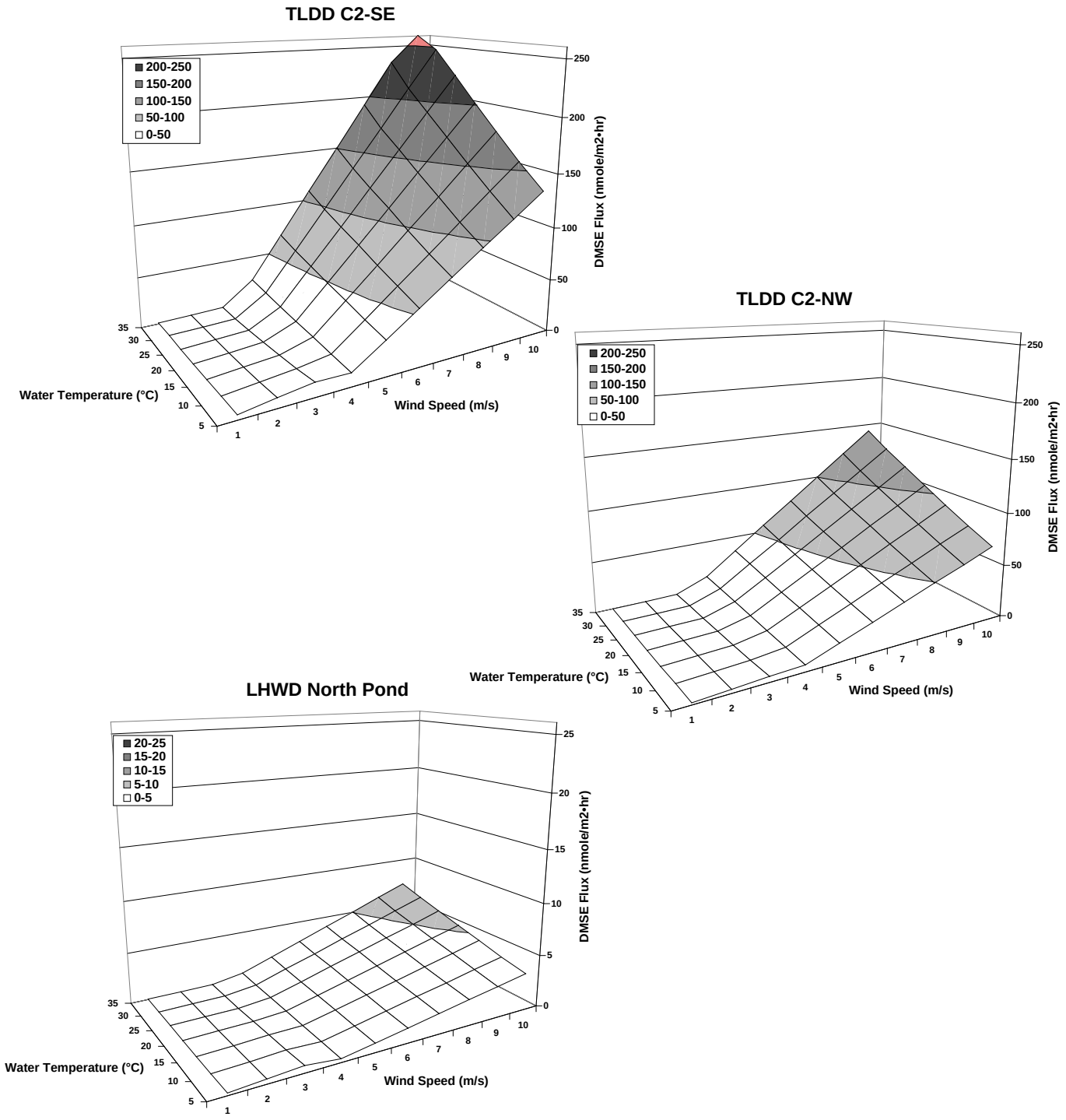

Figure5. Volatilization model of DMSe from two locations in TLDD C2 basin, and LHWD North Pond. The flux model shows the complex relationship imposed on DMSe volatilization by just two factors, wind speed and water temperature. Other factors, such as salinity and microphyte metabolic rate, were not varied. The shaded zones are isopleths of a given flux. Note the differences between two sites in C2 basin; also note that the flux scale for LHWD is 10-fold lower. The site specificity of these relationships (e.g. between two quadrants of C2), and the high likelyhood that these curves change at least seasonally, underscore the need for realtime or continuous monitoring to establish realistic flux estimates.