June 16, 2009

To: Mark H. Capelli, South-Central/Southern Steelhead Recover Coordinator, National Marine Fisheries Service, 735 State Street, Suite 616, Santa Barbara, CA 93101-3351

From: Scott D. Cooper, Professor, Department of Ecology, Evolution, and Marine Biology, University of California, Santa Barbara, CA 93106

Re: Fish Kill in Maria Ygnacio Creek associated with the Jesusita Fire, Santa Barbara County, CA

This memo documents observations and water quality measurements that Sheila Wiseman and I made in Maria Ygnacio Creek, Santa Barbara County, California, on the afternoon of May 14, 2009, subsequent to the Jesusita Fire and a reported fish kill in Maria Ygnacio Creek. I also include a review of the literature on fire retardant effects on rainbow trout.

Field observations and chemical analyses

On Monday, May 11, 2009, I was copied on an email message from Mark Capelli to Ed Keller dealing with the Jesusita Fire. In that message, Mr. Capelli noted that he had just returned from a field trip where he had "examined about a mile of creek between 1900 San Marcos Pass Road and the upper waterfall and found dead *O. mykiss* in virtually every deep hole. Not sure what caused their death, but I collected about a dozen fish for examination." He attached a series of photographs to his message illustrating the habitat and the fish kill.

My area of expertise is stream ecology and I have conducted research on streams in Santa Barbara County for 30 years and advised NMFS on steelhead issues. As a consequence, I followed this message with an email correspondence with Mr. Capelli, obtaining particular information about the fish kill and the name and phone number of the landowner (Mr. Bjorklund) for the affected section of Maria Ygnacio Creek. I called Mr. Bjorklund on Thursday, May 14, and obtained his permission to examine the creek on his property and take water samples. On the afternoon of May 14, Sheila Wiseman and I drove to 1900 San Marcos Pass, checked in with Mr. Bjorklund, then drove down to the creek. We hiked along the 0.75 mile section of Maria Ygnacio Creek from Mr. Bjorklund's picnic area to the high waterfall upstream. The first large pool upstream from the picnic area contained 5 live trout (*Oncorhynchus mykiss*), from 4 – 6 "in length, and two of these were actively feeding on surface insects. The next two pools upstream from this pool also contained live trout, with the uppermost pool of this pair containing one trout approximately 5 " long. From this pool upstream to the waterfall, we saw no more live trout; however, we did see 10 dead trout, of similar size to the live trout in lower pools, including 6 in the pool at the base of the waterfall and 4 in the creek from the waterfall to about a half mile downstream. We also saw a California newt adult (*Taricha torosa*) in one of the pools in the stretch where no live trout were observed. On our hike up the creek we ran into two firefighters from Riverside who had attempted to climb up the canyon to examine a hot spot in the upper Maria Ygnacio basin, but were unable to get to it.

We took two surface water samples (250 ml each), one at the pool at the base of the waterfall and the other in a pool approximately 0.6 mile downstream, both near spots where dead trout were observed. These samples were placed immediately on ice, returned to the laboratory, frozen, then given to UCSB's Marine Science Institute's Analytical Laboratory for analyses of total ammonia, nitrate, and phosphate concentrations using standard APHA procedures. Because Mr. Capelli and Mr. Bjorklund reported Phos-Chek deposits in and near the stream upstream from the waterfall, we focused on total ammonia ($NH_3 + NH_4^+$) and phosphate concentrations as they are dominant Phos-Chek ingredients. The major ingredient in Phos-Chek 259F, which was dropped from helicopters during the Jesusita fire, is diammonium phosphate (> 90% by weight), whereas the major ingredients in Phos-Chek Grade D-75F, the fire retardant dropped by air tankers, are diammonium sulfate (>65% by weight) and diammonium phosphate (>15%). On dissolution in water these compounds break up largely into their ionic forms, ammonium, phosphate, and sulfate. High ammonia concentrations are of particular concern because they are known to be toxic to fish, and the monitoring and control of ammonia concentrations constitutes a major segment of the aquarium and aquaculture businesses. Scientific studies have shown that ammonia is the major fire retardant ingredient having negative effects on aquatic life (Buhl and Hamilton 2000).

The results of chemical analyses of the water from Maria Ygnacio Creek are shown in Table 1. For comparison, I include chemical data from 11 other coastal streams in Santa Barbara County which were collected in late March, 2009. In general, concentrations of total ammonia and phosphate were approximately two orders of magnitude higher in Maria Ygnacio Creek on May 14, 2009, than in other, similar streams in late March. In addition, nitrate concentrations in Maria Ygnacio Creek were, on average, approximately 5 – 6 times higher than in other, similar streams. Because ammonia is highly volatile and we sampled six days after the fish kill and Phos-Chek presence in the stream were first noticed, it is likely that stream ammonia concentrations were much higher right after fire fighting activities in this basin (see below).

Sites	Phosphate (as P, mg/L)	Nitrate + Nitrite (as N, mg/L	Total Ammonia (as N, mg/L)
11 baseline reference sites[a]	0.016 (SE = 0.002, range = 0.010 – 0.037)	0.062 (SE = 0.031, range = 0.002 – 0.32)	0.011 (SE = 0.002, range = 0.003 – 0.024)
Maria Ygnacio Creek, pool just below waterfall	1.98	0.32	1.14
Maria Ygnacio Creek, pool about 0.5 mi below	1.40	0.38	1.00

waterfall			

[a] Romero, San Ysidro, Rattlesnake (upper site unaffected by Tea Fire), Mission (Botanic Gardens and Rocky Nook Park), San Antonio, San Jose (at Trout Club), El Capitan (above cabins), Refugio, Arroyo Hondo, San Onofre Creeks in late March, 2009.

Because a major component of Phos-Chek is diammonium phosphate, total ammonia and phosphate levels in Maria Ygnacio Creek were two orders of magnitude higher than those found in nearby streams unaffected by fire or fire fighting activities, and observers noted Phos-Chek in and around the stream just above the fish kill reach, it seems probable that ammonium and phosphate concentrations were elevated in this stream because of a Phos-Chek drop into the stream. Further, the fish kill was noted immediately after Phos Chek was dropped on a hot spot in the upper Maria Ygnacio basin and occurred downstream of sites where Phos Chek was observed in the stream, so it seems likely that Phos Chek elevated ammonia levels resulting in the fish kill.

Literature on the effects of Phos Chek or ammonium on rainbow trout/steelhead

Most fire retardants commonly dropped on wildfires are composed primarily of ammonia compounds (e.g., diammonium phosphate, diammonium sulfate). Studies have shown that ammonia is the fire retardant component which has the principal negative effects on aquatic life (Buhl and Hamilton 2000). In aqueous solution, total ammonia consists of both un-ionized (NH_3) and ionized (NH_4^+) forms, with the concentrations of each critically dependent on pH and, to a much lesser degree, temperature. Un-ionized ammonia is the form which is toxic to aquatic organisms and the proportions of total ammonia composed of un-ionized ammonia increase as pH increases, so ammonia toxicity generally increases as pH increases. In much of the literature, ammonia concentrations are expressed as total ammonia (i.e., $NH_3 + NH_4^+$); however, un-ionized ammonia concentrations can be calculated from total ammonia concentrations if pH and temperature are also known (Emerson et al. 1975). Besides pH and temperature, ammonia toxicity to fish depends on the ionic composition and concentration of water and dissolved oxygen levels, as well as the species, life stage, size, strain, activity, and feeding rates of fish (Brinkman et al. 2009). Literature information on governmental standards and the negative effects of Phos-Chek or ammonia on rainbow trout is presented in Table 2.

Table 2. Reported values of Phos-Chek or ammonia causing negative effects on rainbow trout (*Oncorhynchus mykiss*) and EPA and California standards for ammonia

Reference	Trout life stage	Response variable	Environmental factors	Phos-Chek, D75F, 259 or 259F (mg/L)	Total ammonia (mg/L)
Smart 1975 cited in Smart 1978	Adults	Median lethal threshold	pH = 6.9, 8.2		205[a], 11[b]
Johnson and Sanders 1977	Swim-up fry	96h LC-50[c]		94 - 165	
Thurston et al. 1981		96h LC-50[c]	pH = 6.8		100
Thurston and Russo 1983	Fry to adults	96h LC-50[c]	T° = 12 – 19°C		11 - 48
Arthur et al. 1987	Variable	96h LC-50[c]	pH = 7.7 – 8.3, T° = 3.6 – 18.7°C		15 - 153
Solbe and Shurben 1989	Egg through fry	LC50[d]	pH = 7.5, T° = 11.5 to 17°C		1.7[e], >26[f]
Gaikowski et al. 1996	Swim-up fry, juveniles (60 d, 90d)	96h LC-50[c]	pH = 7.5[g], 8.2[h] T° = 12°C	218 - 279	6 – 57[g], 0.9 – 28[h]
Buhl and Hamilton 2000	Juveniles (40-d post-hatch)	96h LC-50[c]	pH = 6.8 – 7.3, T° = 12°C	168	39[i], 112[j]
Wicks et al. 2002	Adults (17.8 cm), fry	96h LC-50[c]	pH = 7.0 (adults) or 7.8 (fry), T° = 16.6°C		32[k], 207[l] 17 – 37[m]
Wicks and Randall 2002	Juveniles	96h LC-50[c]	pH = 7.2		174
Brinkman et al. 2009	Swim-up fry	Chronic toxicity, EC20[n]	pH = 7.75, T° = 11.4°C	-	11.2, 5.6[o]
US EPA 1999	Salmonids	CCM[p] CCC[q] CCC[r]			36.4, 5.7, 14.1
CA Regional	COLD	One-hour			3.3[s],

Water Control Board, LA and Central Coast Regions, Basin Plans	waters: salmonids/ other cold water spp. present	average concentration			0.47[t]

[a] pH = 6.9
[b] pH = 8.2
[c] Concentration killing 50% of the fish by 96 hours after the trial starts.
[d] Total mortality as fish progressed from egg through fry stages.
[e] LC50 = 50% of individuals dying through experiment that lasted 73 days. Calculated from Table 1. Started within 24 h of fertilization.
[f] Started with eggs > 24 h after fertilization. Total experiment duration = 49 d.
[g] and [h] Soft[g] (pH = 7.5) versus hard[h] (pH = 8.2) water tested. Results were presented in the paper as un-ionized ammonia concentrations. These were converted to total ammonia concentrations using Emerson et al. (1975)
[i] Total ammonia concentration at the Phos-Chek concentration (168 mg/L) causing 50% mortality over 96 hours.
[j] Total ammonia concentration for ammonium chloride concentration causing 50% mortality over 96 hours.
[k] and [l] Swimming[k] versus resting[l] adults.
[m] 96-h LC-50 for fry over a range of calcium concentrations
[n] Concentration causing a 20% decrease in fish performance (e.g., fish growth).
[o] Corrected to pH = 8
[p] The CMC (acute criterion) was calculated using the following equation for waters where salmonid fish are present: $CMC = (0.275/(1 + 10^{7.204-pH})) + (39.0/(1 + 10^{pH-7.204}))$. This one-hour average concentration of total ammonia nitrogen (in mg N/L) will not be exceeded more than once every three years on average. Calculated pH and temperature for Maria Ygnacio Creek at time of fish kill = 8.3 and 15°C.
[q] The CCC (chronic criterion) was calculated using the following equation for waters where fish early life stages are present: $CCC = ((0.0577/(1 + 10^{7.688-pH})) + (2.487/(1 + 10^{pH-7.688}))) \times MIN(2.85, 1.45 \cdot 10^{0.028 \cdot (25-T)})$. This 30-day average concentration should not be exceeded more than once every three years on average.
[r] In addition, the highest four-day average within the 30-day period should not exceed 2.5 times the CCC.
[s] California Regional Water Quality Control Board, Los Angeles Region, Basin Plan for the Coastal Watersheds of Los Angeles and Ventura Counties. The Basin Plan presents a table of total ammonia impairment thresholds for different pHs and temperatures. The estimated threshold total ammonia concentration is for a pH of 8.25 and a temperature of 15°C.
[t] California Regional Water Quality Control Board, Central Coast Region, Basin Plan states "the discharge of wastes shall not cause concentrations of unionized ammonia (NH_3) to exceed 0.025 mg/l (as N) in receiving waters". At a pH of 8.3 and a temperature of 15°C, this equals a total ammonia concentration (as N) of 0.47 mg/L.

Concentrations of Phos-Chek which kill 50% of rainbow trout individuals over 96 hours (96h LC-50) ranged from approximately 100 to 300 mg/L across studies, whereas total ammonia concentrations which killed 50% of rainbow trout over 96 hours ranged from approximately 1 – 200 mg/L. The large variation in 96hr LC-50 values for total ammonia was related, to a large degree, to pH, with higher values recorded at lower pH's (ca. 7) and lower values recorded at higher pH's (ca. 8). For example, Smart (1978, citing Smart 1975) reported median lethal total ammonia thresholds for rainbow trout to be 205 mg/L at pH 6.9 and 11 mg/L at pH 8.2. In addition, the ammonia concentrations associated with 96h LC-50 values for Phos-Chek may have been influenced by the toxic effects of other Phos-Chek ingredients (such as corrosion inhibitors, coloring agents, etc.). The 96-h LC50 values listed for rainbow trout fry and fingerlings on the Material Safety Data Sheet provided by the USFS for Phos-Chek 259F (115 and 160 mg/L Phos Check) are within the range of values reported in the literature; however, the 96-h LC50 values for rainbow trout reported on the Material Safety Data Sheet for Phos-Chek D-75F (> 1000 mg/L) are clearly in error, being approximately an order of magnitude higher than Phos-Check 96-h LC50 values reported in the literature. Because the molecular weights of the principal ingredients of Phos-Chek 259F (diammonium phosphate) and Phos-Chek D-75F (diammonium sulfate) are similar and the principal toxic agent in both formulations is ammonia, the 96-h LC 50 values for both types of Phos-Chek should be similar; a contention supported by the literature reviewed in Table 1.

The results in Table 1 carry considerable uncertainty and are likely to be conservative because they are based on laboratory bioassays. As has been noted by several researchers, it is not clear to what degree laboratory bioassays replicate and have relevance to field conditions. Ammonia toxicity is influenced by the concentrations of major ions and dissolved oxygen, but congruence in the chemical composition of water between laboratory and field situations is usually uncertain. Further, following standard EPA procedures, laboratory bioassays are usually performed under static conditions using resting, starved, and unstressed fish, all of which are usually unrepresentative of flowing stream conditions where fish are active, feeding, and stressed (Randall and Tsui 2002). Finally, laboratory trials usually are performed on hatchery trout which, because they are reared under crowded conditions, probably can tolerate higher ammonia concentrations than wild trout (Brinkman et al. 2009). Because internal ammonia levels in fish increase with increased feeding, swimming, and stress levels, and because hatchery trout likely can tolerate higher ammonia concentrations than wild trout, it is likely that the 96 hr LC50 values listed in Table 1 are higher than the actual 96 hr LC50 values applicable to wild trout in their natural environment.

The Material Safety Data Sheets for these Phos-Chek formulations also are misleading because they list both forms of Phos-Chek as being "practically nontoxic" based on reported 96-hr LC50 values. Given the vast hatchery, aquaculture, aquarium, and fisheries literature on the toxic effects of ammonia on fish and on ways to mitigate ammonia impacts, it is very puzzling that Phos-Chek is listed as being practically nontoxic to aquatic life. Conclusions of the toxicity of a material depend on both concentrations of the major toxic component (e.g., ammonia) occurring in affected water bodies, as well as on the concentration of this component which kills aquatic organisms. Buhl and Hamilton (2000) reported that Phos-Chek 259F is mixed at the ratio of 1 gal. to 4.25 gal. of water creating a solution with a Phos-Chek concentration of 136,617 mg/L whereas Phos-Chek D75-F is usually mixed to create a solution of 143,800 mg/L Gaikowski et al. 1996). Direct Phos-Chek drops into water bodies, then, would need to be diluted about 2 - 3 orders of magnitude (ca. 500 - 800 X) to reduce concentrations to 96-hr LC 50 levels (Gaikowski et al. 1996, Buhl and Hamilton 2000). Because 96-hr LC 50 values deal with concentrations directly lethal to the majority of fish, higher dilution factors are needed to reduce concentrations to levels which have no impact on any trout (1700 X dilution to reduce to concentrations with no acute effects (NAEC, 0 % mortality at 96 hrs.), Buhl and Hamilton 2000). Because fire retardants are applied as highly concentrated solutions, Gaikowski et al. (1996) concluded that "the possibility of concentrations close to the 96-h LC50 in the environment are real and render the terms "practically" and "relatively harmless" in this scenario to be irrelevant". Although the Material Safety Data Sheets use the Passino and Smith (1987) system to develop their hazard ranking ("practically nontoxic") for each material, this system does not appear to be applicable when fire retardants directly hit or enter streams.

Through direct measurements and simulation modeling of fire retardant drops into streams, USFS researchers Norris and Webb (1989) concluded that "direct application of retardant to many streams is likely to cause fish mortality". Direct application of retardant (composed primarily of ammonium phosphate) to the Eastern Fork San Dimas Canyon Creek, southern California, resulted in peak total ammonia concentrations of 30 mg/L within half an hour at a site 45 m downstream of the application site; however, ammonia concentrations rapidly dissipated through time and downstream. For example, peak ammonia concentrations 45 m below the application site were reduced 100 fold by 25 minutes after the application, and were reduced to 19% and 4 % of peak values at 200 m and 400 m below the application site. Although ammonia is highly volatile and rapidly degrades to nitrate via bacterial action, and ammonia in Phos-Chek is quickly diluted by flowing water, small creeks in southern California often have very low summer flows (down to 1 – 2 L/s; San Dimas Creek = 7.1 L/s at the time of the Norris and Webb study) and trout responses to high ammonia levels are often immediate. Trout mortality in most of the studies listed in Table 1 occurred almost immediately (< 24 hours) when Phos-Chek or ammonia concentrations reached lethal levels (i.e., 24-hr LC50's = 96-hr LC50's). Given the 2000-fold dilution in total ammonia concentrations recorded within 12 hours at 45 m below the retardant application site in the East Fork San Dimas Creek by Norris and Webb (1989) and the ca. 1 mg/L total ammonia concentrations that we measured in Maria Ygnacio Creek approximately 6 days after the retardant drop, it is clear that ammonia concentrations immediately after retardant application in Maria Ygnacio Creek were at least an order of magnitude higher than lethal limits recorded for rainbow trout. These conclusions will be tested by analyses of the water samples collected by Mark Capelli and Robert Bjorklund, provided samples are not stored too long before analyses.

Conclusions

Fish kills during or immediately following fire-fighting activities have been reported throughout the western U.S. and Alaska, and have usually been attributed to aerial application of ammonium-based retardants resulting in direct drops of retardant into streams (Norris and

Webb 1989, Minshall et al. 1989, Minshall and Brock 1991, Buhl and Hamilton 2000, Dunham et al. 2003). Based on measurements of total ammonia concentrations in Maria Ygnacio Creek approximately six days after retardant drops in its basin, ammonia dilution rates associated with a pulse application of retardant to another southern California stream, and a review of lethal limits of Phos-Chek and ammonia for rainbow trout, I conclude that Phos-Chek and associated ammonia levels in Maria Ygnacio Creek immediately after Phos-Chek drops into the creek likely exceeded rainbow trout lethal limits, causing the fish kill in Maria Ygnacio Creek. Further, observations that the fish kill was downstream of sites containing Phos-Chek deposits and occurred almost immediately after Phos-Chek drops into this canyon, reinforce this conclusion. It is unlikely that there were any direct effects of the fire on trout in this stream, because the fish kill reach was not burned and other studies have shown no effect of ash leachate on trout populations (Minshall and Brock 1991).

Planning

Climate models predict that southern California will experience more prolonged droughts, lower stream flows, and more frequent and intense fires into the foreseeable future. Because streams in southern California typically have low flows and some of the organisms occupying perennial streams, such as rainbow trout/steelhead, are at the southern edge of their geographical ranges and are particularly sensitive to stream warming and drying, it is likely that climate change will have large impacts on stream ecosystems in southern California. Increased drying and higher temperatures, as well as the ever increasing interface between urban and wild lands, will result in an increased incidence of fire and fire-fighting activities. Given the steep terrain in many parts of southern California, aerial application of fire retardants is often the only effective way of combating fires; however, direct drops of ammonia-based fire retardants into streams can have negative direct impacts on stream organisms, particularly trout which are sensitive to many toxicants (including retardants and associated ammonia). Further, many southern California streams have hard waters and relatively high pH's (median for 11 Santa Barbara streams similar to Maria Ygnacio Creek = 8.3), and ammonia toxicity increases with pH, so ammonia concentrations causing fish death in these streams can be relatively low. Because of the small size of many southern California streams, listed trout populations are often small, so are particularly vulnerable to toxicant effects. Further, small, perennial streams in southern California are particularly sensitive to retardant drops because their low flows minimize the dilution of associated toxicants.

In general, then, in southern California the small size, low flows, hard waters, and high pH's of many perennial streams, high incidence of fire and fire-fighting activities, and the high sensitivity of trout to drying, warming, and toxicants, make rainbow trout/steelhead populations particularly vulnerable to fire retardant applications. Although Norris and Webb

(1989) concluded that retardant application to upland and riparian zones would likely have little effect on fish mortality owing to the rapid loss or degradation of ammonia, they also concluded that direct retardant application to streams would result in fish kills. Through their simulation models, they concluded that fire retardant impacts on stream organisms would depend on application and stream characteristics (e.g., application perpendicular or parallel to stream flow, the width, depth, and flow rates of streams, stream geomorphology (pool/riffle ratios), and the density of the riparian canopy). They pleaded for effective fire-fighting plans which minimized impacts to the environment by (1) identifying stream sections which need to be protected, including those supporting rare or endangered species and (2) developing fire fighting plans, including the use of retardants, which minimize impacts to sensitive streams. Given the presence of listed southern steelhead/rainbow trout in small southern California streams which drain steep basins covered by fire-prone chaparral and forest ecosystems, natural resource managers need to identify the streams that contain steelhead/trout populations then develop fire-fighting plans that prohibit the application of retardants in or near sensitive streams. Although the USFS has guidelines for avoiding retardant drops near or in sensitive stream zones, a margin of error needs to be incorporated into these guidelines and guidelines need to be followed.

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